

PRINCIPLES AND PRACTICES OF BIOVENTING

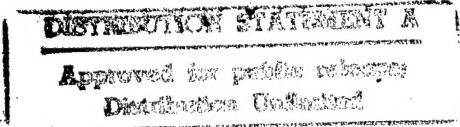
VOLUME I: BIOVENTING PRINCIPLES

by

**Andrea Leeson and Robert E. Hinchee
Battelle Memorial Institute
Columbus OH**

with contributions by

**Bruce A. Alleman, Douglas C. Downey, Gregory Headington,
Jeffrey A. Kittel, Priti Kumar, Lt Colonel Ross N. Miller, Say Kee Ong,
Gregory D. Sayles, Lawrence Smith, Catherine M. Vogel**



19970425 024

for

**Catherine M. Vogel
Environics Directorate of
the Armstrong Laboratory
Tyndall AFB FL**

**Gregory D. Sayles
National Risk Management
Research Laboratory
U.S. Environmental
Protection Agency
Cincinnati OH**

**Lt Colonel Ross N. Miller
U.S. Air Force Center for
Environmental Excellence
Technology Transfer Division
Brooks AFB TX**

| DMC QUALITY INSPECTED 8

This report is a work prepared for the United States Government by Battelle. In no event shall either the United States Government or Battelle have any responsibility or liability for any consequences of any use, misuse, inability to use, or reliance upon the information contained herein, nor does either warrant or otherwise represent in any way the accuracy, adequacy, efficacy, or applicability of the contents hereof. The methods presented in this document are ones used by the U.S. Air Force and the U.S. Environmental Protection Agency, but are not necessarily the only methods available.

TABLE OF CONTENTS

LIST OF TABLES	iii
LIST OF FIGURES	iv
LIST OF EXAMPLES	vii
ABBREVIATIONS AND ACRONYMS	viii
SYMBOLS USED IN CALCULATIONS	viii
1.0 INTRODUCTION	2
2.0 DEVELOPMENT OF BIOVENTING	6
2.1 Oxygen Supply to Contaminated Areas	6
2.2 Bioventing Research and Development	9
2.3 Structure of Bioventing Initiative Field Treatability Studies and Bioventing System Design	17
2.4 Emerging Techniques for Modifications to Bioventing Systems	18
3.0 PRINCIPLES OF BIOVENTING	20
3.1 Physical Processes Affecting Bioventing	20
3.1.1 Soil Gas Permeability	20
3.1.2 Contaminant Distribution	23
3.1.3 Oxygen Radius of Influence	30
3.2 Microbial Processes Affecting Bioventing	31
3.2.1 Microbial Kinetics	31
3.2.2 Environmental Parameters Affecting Microbial Processes	33
3.2.2.1 Electron Acceptor Conditions	34
3.2.2.2 Moisture Content	35
3.2.2.3 Soil pH	41
3.2.2.4 Soil Temperature	41
3.2.2.5 Nutrient Supply	46
3.2.2.6 Contaminant Concentration	53
3.2.2.7 Bioavailability and Relative Biodegradability	56
3.3 Compounds Targeted for Removal	56
3.4 BTEX Versus TPH Removal in Petroleum-Contaminated Soils	60
4.0 BIOVENTING CASE HISTORIES	63

4.1	Site 914, Hill AFB, Utah	63
4.2	Tyndall AFB, Florida	68
4.3	280, Hill AFB, Utah	71
4.4	Site 20, Eielson AFB, Alaska	74
4.5	Fire Training Area, Battle Creek ANGB, Michigan	85
5.0	ANALYSES OF BIOVENTING INITIATIVE RESULTS	90
5.1	Estimate of Contaminant Removal at Bioventing Initiative Sites	91
5.2	Statistical Analysis of Bioventing Initiative Data	98
5.2.1	Procedures for Statistical Analysis	98
5.2.2	Calculation of Oxygen Utilization and Carbon Dioxide Production Rates	100
5.2.3	Correlation of Oxygen Utilization Rates and Environmental Parameters	104
5.2.4	Correlation of Oxygen Utilization and Carbon Dioxide Production Rate Ratios With Environmental Parameters	113
5.2.5	Correlation of Soil Gas Permeability With Environmental Parameters	116
5.2.6	Analyses of Data From Contaminated and Background Areas	120
5.2.7	Summary	120
6.0	REFERENCES	122
APPENDIX A:	GLOSSARY	A-1
APPENDIX B:	DATA FROM BIOVENTING INITIATIVE SITES	B-1

LIST OF TABLES

Table 2-1.	Oxygen Requirements Based on Supplied Form of Oxygen	8
Table 2-2.	Summary of Reported In Situ Respiration Rates and Bioventing Data	15
Table 3-1.	Values for Key Properties of Select Petroleum Hydrocarbons	28
Table 4-1.	Cost Analysis of Soil Warming Techniques at Site 20, Eielson AFB, Alaska	82
Table 5-1.	Data Parameters Included in the Statistical Analyses	101
Table 5-2.	Parameters That Distinguish the Seven Sites with High Oxygen Utilization Rates From the Remaining Sites	105

LIST OF FIGURES

Figure 1-1.	Hydrocarbon Distribution at a Typical Contaminated Site	3
Figure 1-2.	Schematic Diagram of a Typical Bioventing System	4
Figure 2-1.	Historical Perspective of the Development of Bioventing	10
Figure 2-2.	Locations of Bioventing Initiative Sites	14
Figure 3-1.	Distribution of Silt- and Clay-Sized Particles at Bioventing Initiative Sites	22
Figure 3-2.	Sorption Isotherms	26
Figure 3-3.	Relationship Between Sorbed Contaminant Concentration and Vapor- or Aqueous-Phase Concentrations	29
Figure 3-4.	Soil Moisture Content Measurements at Bioventing Initiative Sites	36
Figure 3-5.	Direct Correlation Between Oxygen Utilization Rates and Soil Moisture Content at Bioventing Initiative Sites	37
Figure 3-6.	Oxygen and Carbon Dioxide Concentrations Prior to and After Irrigation at Twentynine Palms, California	38
Figure 3-7.	Soil pH Measurements at Bioventing Initiative Sites	42
Figure 3-8.	Correlation Between Oxygen Utilization Rate and Soil pH at Bioventing Initiative Sites	43
Figure 3-9.	Soil Temperature Versus Biodegradation Rate at Site 20, Eielson AFB, Alaska . .	45
Figure 3-10.	TKN Measurements at Bioventing Initiative Sites	49
Figure 3-11.	Correlation Between Oxygen Utilization Rate and TKN at Bioventing Initiative Sites	50
Figure 3-12.	Total Phosphorus Measurements at Bioventing Initiative Sites	51
Figure 3-13.	Correlation Between Oxygen Utilization Rate and Total Phosphorus at Bioventing Initiative Sites	52
Figure 3-14.	Iron Concentration Measurements at Bioventing Initiative Sites	54
Figure 3-15.	Correlation Between Oxygen Utilization Rates and Iron Content at Bioventing Initiative Sites	55
Figure 3-16.	Relationship Between Contaminant Physicochemical Properties and Potential for Bioventing	58
Figure 3-17.	Relationship Between Contaminant Vapor Pressure and Aerobic Biodegradability	59
Figure 3-18.	Results of Soil Analysis Before and After Venting from Plot V2 at Tyndall AFB, Florida	61
Figure 3-19.	Contaminant Distribution at Bioventing Initiative Sites	62
Figure 4-1.	Cumulative Hydrocarbon Removal and the Effect of Moisture and Nutrient Addition at Site 914, Hill AFB, Utah	65
Figure 4-2.	Results of Soil Analysis Before and After Treatment at Site 914, Hill AFB, Utah	67
Figure 4-3.	Cumulative Percent Hydrocarbon Removal and the Effect of Moisture and Nutrient Addition at Tyndall AFB, Florida	70
Figure 4-4.	Schematic Diagram Showing Locations of Soil Gas Monitoring Points, Surface Monitoring Points, and Injection Wells at Site 280, Hill AFB, Utah	72
Figure 4-5.	Geologic Cross Section Showing Known Geologic Features and Soil TPH Concentrations (mg/kg) at Site 280, Hill AFB, Utah	73
Figure 4-6.	Site Average Initial and Final BTEX Soil Sample Results at Site 280, Hill AFB, Utah	75

Figure 4-7.	Site Average Initial and Final TPH Soil Sample Results at Site 280, Hill AFB, Utah	76
Figure 4-8.	Cross Section Showing Geologic Features and Typical Construction Details of the Active Warming Test Plot, Site 20, Eielson AFB, Alaska	78
Figure 4-9.	Soil Temperature in Four Test Plots and the Background Area at Site 20, Eielson AFB, Alaska	79
Figure 4-10.	Biodegradation Rates in Four Test Plots at Site 20, Eielson AFB, Alaska	80
Figure 4-11.	Site Average Initial and Final BTEX Soil Sample Results at Site 20, Eielson AFB, Alaska	83
Figure 4-12.	Site Average Initial and Final TPH Soil Sample Results at Site 20, Eielson AFB, Alaska	84
Figure 4-13.	Hydrogeologic Cross Section of the Fire Training Area, Battle Creek ANGB, Michigan (Engineering Science, 1992)	86
Figure 4-14.	Initial and Final Soil Gas Concentrations at the Fire Training Area, Battle Creek, Michigan	88
Figure 4-15.	Initial and Final Soil Concentrations at the Fire Training Area, Battle Creek, Michigan	89
Figure 5-1.	Soil Gas BTEX Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data	92
Figure 5-2.	Soil Gas TPH Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data	93
Figure 5-3.	Soil BTEX Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data	94
Figure 5-4.	Soil TPH Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data	95
Figure 5-5.	Average Soil and Soil Gas BTEX and TPH Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data	96
Figure 5-6.	Initial and Final Soil Sampling Results at Site 3, Battle Creek ANGB, Michigan	97
Figure 5-7.	Average BTEX Concentrations at Bioventing Initiative Sites	99
Figure 5-8.	Use of Piecewise Analysis of Oxygen Utilization Data from Site FSA-1, AFP 4, Texas	103
Figure 5-9.	Oxygen Utilization Rates, Oxygen:Carbon Dioxide Rate Ratios, Element Concentrations, Moisture Content, pH, and Alkalinity Site Average Correlation Scatterplot	106
Figure 5-10.	Oxygen Utilization Rates, Oxygen:Carbon Dioxide Rate Ratios, Contaminant Concentrations, Temperature, and Moisture Content Site Average Correlation Scatterplot	107
Figure 5-11.	Oxygen Utilization Rates, Oxygen:Carbon Dioxide Rate Ratios, Particle Size, Moisture Content, and Soil Gas Permeability Site Average Correlation Scatterplot	108
Figure 5-12.	Element Concentrations and Particle Size Site Average Correlation Scatterplot	109
Figure 5-13.	Contaminant Concentrations and Particle Size Site Average Correlation Scatterplot	110
Figure 5-14.	pH, Alkalinity, and Particle Size Site Average Correlation Scatterplot	111
Figure 5-15.	Actual Versus Model-Predicted Oxygen Utilization Rates	114
Figure 5-16.	Variation of pH and the Effect on Oxygen Utilization to Carbon Dioxide Rate Ratio Based on Model Predictions With Average Levels of Other Parameters	117

Figure 5-17.	Soil Gas Permeability, Moisture Content, and Particle Size Site Average Correlation Scatterplot	118
Figure 5-18.	Variation of Clay and the Effect on Soil Gas Permeability Based on Model Predictions	119

LIST OF EXAMPLES

Example 2-1.	Calculation of Air-Saturated Water Mass That Must Be Delivered to Degrade Hydrocarbons	7
Example 3-1.	Moisture Content Change During Air Injection and Water Generated During Biodegradation	39
Example 3-2.	Calculation of the van't Hoff-Arrhenius Constant From Site Data	44
Example 3-3.	Estimation of Nutrient Requirements In Situ	47

ABBREVIATIONS AND ACRONYMS

AFB	Air Force Base
AFCEE	U.S. Air Force Center for Environmental Excellence
AFP	Air Force Plant
AFS	Air Force Station
AL/EQ	Armstrong Laboratory Environics Directorate
ANGB	Air National Guard Base
BTEX	benzene, toluene, ethylbenzene, and xylenes
cfm	cubic ft per minute
DNAPL	dense, nonaqueous-phase liquid
LNAPL	less dense, nonaqueous-phase liquid
NAS	Naval Air Station
NLIN	nonlinear regression procedure
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
RD&A	Research, Development, and Acquisition
R _i	radius of influence
SAS	Statistical Analysis System
SVE	soil vacuum extraction
TCE	trichloroethylene
TKN	total Kjeldahl nitrogen
TPH	total petroleum hydrocarbon
TVH	total volatile hydrocarbon
UST	underground storage tank
U.S. EPA	U.S. Environmental Protection Agency
VOC	volatile organic carbon

SYMBOLS USED IN CALCULATIONS

C _s	quantity sorbed to the solid matrix
C _v	volumetric concentration in the vapor phase
C _{vsat}	saturated vapor concentration
C _w	volumetric concentration in the aqueous phase
E _a	activation energy
f _{oc}	organic carbon fraction
k	maximum rate of substrate utilization
k _d	endogenous respiration rate
k _o	baseline biodegradation rate
k _B	biodegradation rate
K _d	sorption coefficient
K _{ow}	octanol/water partition coefficient
K _S	Monod half-velocity constant
k _T	temperature-corrected biodegradation rate
MW	molecular weight
P _V	vapor pressure of pure contaminant at temperature T

Q	flowrate
R	gas constant
R_I	radius of influence
S	concentration of the primary substrate (contaminant)
s_x	solubility in water
t	time
T_{abs}	absolute temperature ($^{\circ}\text{K}$)
x	mole fraction
X	concentration of microorganisms
Y	cell yield

ACKNOWLEDGEMENTS

The authors would like to thank the following people for serving as peer reviewers for this document: R. Ryan Dupont, Ph.D., Utah State University; Jack van Eyk, Ph.D., Delft Geotechnic; Paul Johnson, Ph.D., Arizona State University, and Chi-Yuan Fan, U.S. EPA National Risk Management Laboratory.

The authors also would like to thank the following people for their help in finishing this document: Amanda Bush, Dr. Gordon Cobb, Rhonda Copley, Lynn Copley-Graves, Dean Foor, Jim Gibbs, Patrick Haas, Wendy Huang, Gina Melaragno, Christine Peterson, Carol Young, and Dr. George Yu.

VOLUME I: BIOVENTING PRINCIPLES

This document is a product of the bioventing research and development efforts sponsored by the U.S. Air Force Armstrong Laboratory, the Bioventing Initiative sponsored by the U.S. Air Force Center for Environmental Excellence (AFCEE) Technology Transfer Division, and the Bioremediation Field Initiative sponsored by the U.S. Environmental Protection Agency (U.S. EPA).

The Armstrong Laboratory Environics Directorate (AL/EQ), an element of the Air Force Human Systems Center, began its research and development program in bioventing in 1988 with a study at Hill Air Force Base (AFB), Utah. Follow-on efforts included field research studies at Tyndall AFB, Florida, Eielson AFB, Alaska, and F.E. Warren AFB, Wyoming, to monitor and optimize process variables. Results from these research efforts led to the Bioventing Initiative and are discussed in this document.

The AFCEE's Bioventing Initiative has involved conducting field treatability studies to evaluate bioventing feasibility at more than 125 sites throughout the United States. At those sites where feasibility studies produced positive results, pilot-scale bioventing systems were installed and operated for 1 year. Results from these pilot-scale studies have culminated in production of this document.

The U.S. EPA's Bioremediation Field Initiative was established to provide the U.S. EPA and state project managers, consulting engineers, and industry with timely information regarding new developments in the application of bioremediation at hazardous waste sites. This program has sponsored field research to enable the U.S. EPA laboratories to more fully document newly developing bioremediation technologies. As part of the U.S. EPA Bioremediation Field Initiative, the U.S. EPA has contributed to the Air Force Bioventing Initiative in the development of the test plan for conducting the pilot-scale bioventing studies and assisted in the development of this manual.

The results from bioventing research and development efforts and from the pilot-scale bioventing systems have been used to produce this two-volume manual. Although this design manual has been written based on extensive experience with petroleum hydrocarbons (and thus, many examples use this contaminant), the concepts here should be applicable to any aerobically biodegradable compound. The manual provides details on bioventing principles; site characterization; field treatability studies; system design, installation, and operation; process monitoring; site closure; and optional technologies to combine with bioventing if warranted. This first volume describes the basic principles of bioventing. The second volume focuses on bioventing design and process monitoring.

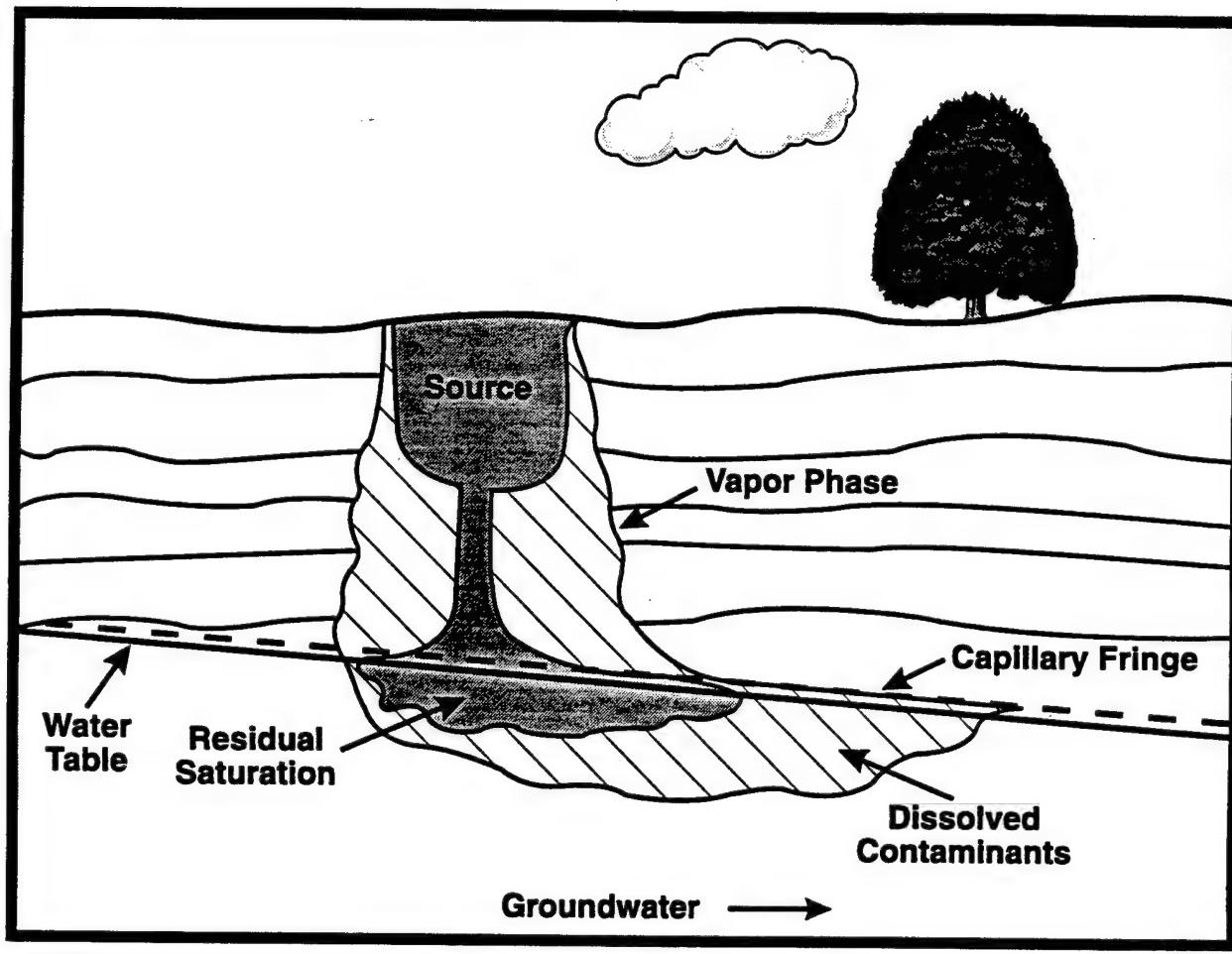
1.0 INTRODUCTION

Bioventing is the process of aerating soils to stimulate *in situ* biological activity and promote bioremediation. Bioventing typically is applied *in situ* to the vadose zone and is applicable to any chemical that can be aerobically biodegraded, but to date has been implemented primarily at petroleum-contaminated sites. Through the efforts of the U.S. Air Force Bioventing Initiative and the U.S. EPA Bioremediation Field Initiative, bioventing has been implemented at more than 150 sites and has emerged as one of the most cost-effective and efficient technologies currently available for vadose zone remediation of petroleum-contaminated sites. This document is a culmination of the experience gained from these sites and provides specific guidelines on the principles and practices of bioventing.

Much of the hydrocarbon residue at a fuel-contaminated site is found in the vadose zone soils, in the capillary fringe, and immediately below the water table (Figure 1-1). Seasonal water table fluctuations typically spread residues in the area immediately above and below the water table. Conventional physical treatment in the past involved pump-and-treat systems where groundwater was pumped out of the ground, treated, and either discharged or reinjected. Although useful for preventing continued migration of contaminants, these systems rarely achieved typical cleanup goals. Bioventing systems are designed to remove the contaminant source from the vadose zone, thereby preventing future and/or continued contamination of the groundwater.

A typical bioventing system is illustrated in Figure 1-2. Although bioventing is related to the process of soil vacuum extraction (SVE), the primary objectives of these two bioremediation technologies are different. Soil vacuum extraction is designed and operated to maximize the volatilization of low-molecular-weight compounds, with some biodegradation occurring. In contrast, bioventing is designed to maximize biodegradation of aerobically biodegradable compounds, regardless of their molecular weight, with some volatilization occurring. The major distinction between these technologies is that the objective of soil venting is to optimize removal by volatilization, while the objective of bioventing is to optimize biodegradation while minimizing volatilization and capital and utility costs. Although both technologies involve venting of air through the subsurface, the differences in objectives result in different design and operation of the remedial systems.

The following chapters provide an overview of the principles of bioventing in relation to physical, chemical, and microbial processes occurring in the field. An overview of the development of bioventing, including development of the Bioventing Initiative is provided as a basis for the data



CD\Lesson\31-1

Figure 1-1. Hydrocarbon Distribution at a Typical Contaminated Site

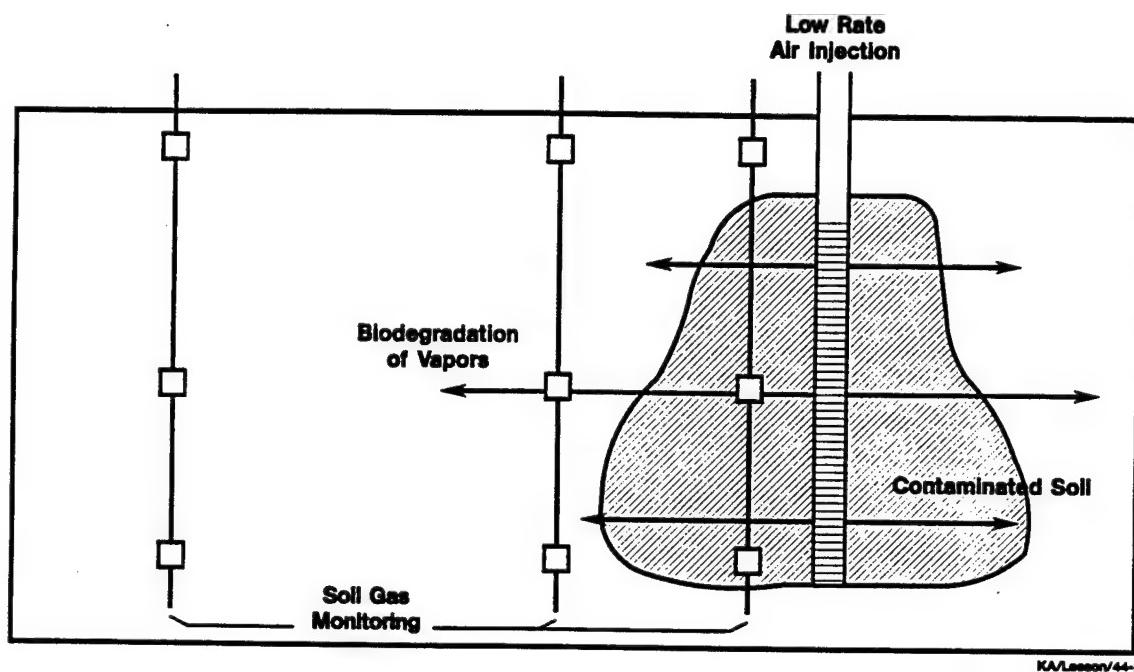


Figure 1-2. Schematic Diagram of a Typical Bioventing System

presented in this document. Data from Bioventing Initiative sites are used throughout this document to illustrate principles of bioventing as determined from field testing.

2.0 DEVELOPMENT OF BIOVENTING

This chapter is intended to provide a framework for this document, describing the development and structure of the Bioventing Initiative and, ultimately, this document. This chapter provides an overview of bioventing, covering oxygen supply *in situ* — the dominant issue in the evolution of bioventing, early bioventing studies which led to development of the Bioventing Initiative, the final structure of treatability studies and bioventing system design used for the Bioventing Initiative and, finally, emerging techniques that are being investigated as modifications to the conventional bioventing design described in this document.

2.1 Oxygen Supply to Contaminated Areas

One of the main driving forces behind the development of bioventing was the difficulty in delivering oxygen *in situ*. Many contaminants, especially the petroleum hydrocarbons found in fuels, are biodegradable if oxygen is available. Traditionally, enhanced bioreclamation processes used water to carry oxygen or an alternative electron acceptor to the contaminated zone. This was common whether the contamination was present in the groundwater or in the unsaturated zone. Media for adding oxygen to contaminated areas have included pure oxygen-sparged water, air-sparged water, hydrogen peroxide, and air.

In all cases where water is used, the solubility of oxygen is the limiting factor. At standard conditions, a maximum of 8 to 10 mg/L of oxygen can be obtained in water when aerated, while 40 to 50 mg/L can be obtained if sparged with pure oxygen, and up to 500 mg/L of oxygen theoretically can be supplied utilizing 1,000 mg/L of hydrogen peroxide. Using the stoichiometric equation shown as Equation (2-1)¹, the quantity of water which must be delivered to provide sufficient oxygen for biodegradation can be calculated.



An example of calculating the mass of water that must be delivered for hydrocarbon degradation is shown in Example 2-1. Table 2-1 summarizes oxygen requirements based on the supplied form of oxygen.

¹ Refer to Section 3.2 for development of this equation.

Example 2-1. Calculation of Air-Saturated Water Mass That Must Be Delivered to Degrade Hydrocarbons: Based on Equation (2-1), the stoichiometric molar ratio of hydrocarbon to oxygen is 1:9.5. Or, to degrade one mole of hydrocarbons, 9.5 moles of oxygen must be consumed. On a mass basis:

$$\frac{1 \text{ mole C}_6\text{H}_{14}}{9.5 \text{ moles O}_2} \times \frac{1 \text{ mole O}_2}{32 \text{ g O}_2} \times \frac{86 \text{ g C}_6\text{H}_{14}}{1 \text{ mole C}_6\text{H}_{14}} = \frac{86 \text{ g C}_6\text{H}_{14}}{304 \text{ g O}_2} = \frac{1 \text{ g C}_6\text{H}_{14}}{3.5 \text{ g O}_2}$$

Given an average concentration of 9 mg/L oxygen dissolved in water, the amount of air-saturated water that must be delivered to degrade 1 g hydrocarbon is calculated as follows:

$$\frac{\frac{3.5 \text{ g O}_2 \text{ required}}{9 \text{ mg O}_2 \times \frac{1 \text{ g}}{1 \text{ L H}_2\text{O}}} = \frac{390 \text{ L H}_2\text{O}}{1 \text{ g C}_6\text{H}_{14}}}{1,000 \text{ mg}}$$

or, to degrade 1 lb:

$$\frac{390 \text{ L H}_2\text{O}}{1 \text{ g C}_6\text{H}_{14}} \times \frac{1 \text{ gallon}}{3.8 \text{ L}} \times \frac{1,000 \text{ g}}{2.2 \text{ lb}} = \frac{47,000 \text{ gallons H}_2\text{O}}{1 \text{ lb C}_6\text{H}_{14}}$$

Due to the low aqueous solubility of oxygen, hydrogen peroxide has been tested as an oxygen source in laboratory studies and at several field sites (Hinchee et al., 1991a; Aggarwal et al., 1991; Morgan and Watkinson, 1992). As shown in Table 2-1, if 500 mg/L of dissolved oxygen can be supplied via hydrogen peroxide, the mass of water that must be delivered is reduced by more than an order of magnitude. Initially, these calculations made the use of hydrogen peroxide appear to be an attractive alternative to injecting air-saturated water.

Hydrogen peroxide is miscible in water and decomposes to release water and oxygen as shown in Equation (2-2):



Many substances commonly present in groundwater and soils act as catalysts for the decomposition of peroxide. Important among these are aqueous species of iron and copper, and the enzyme catalase (Schumb et al., 1955), which has significant activity in situ (Spain et al., 1989). If

Table 2-1. Oxygen Requirements Based on Supplied Form of Oxygen

Oxygen Form	Oxygen Concentration in H ₂ O	Volume to Degrade 1 lb Hydrocarbon
Air-saturated H ₂ O	8 to 10 mg/L	47,000 gallons (180,000 L)
Oxygen-saturated H ₂ O	40 to 50 mg/L	11,000 gallons (42,000 L)
Hydrogen peroxide	Up to 500 mg/L	1,600 gallons (6,100 L)
Air	NA (21% vol/vol in air)	170 ft ³ (4,800 L)

the rate of oxygen formation from hydrogen peroxide decomposition exceeds the rate of microbial oxygen utilization, gaseous oxygen may form due to its limited aqueous solubility. Gaseous oxygen may form bubbles that may not be transported efficiently in groundwater, resulting in ineffective oxygen delivery.

Phosphate is commonly used in nutrient formulations in an effort to decrease the rate of peroxide decomposition in groundwater applications (Britton, 1985). However, the effectiveness of phosphate addition in stabilizing peroxide injected into an aquifer has not been well established and conflicting results have been reported by different researchers (American Petroleum Institute, 1987; Brown et al., 1984; Downey et al., 1988; Huling et al., 1990; Morgan and Watkinson, 1992).

A field experiment was conducted by Hinchee et al. (1991a) to examine the effectiveness of hydrogen peroxide as an oxygen source for in situ biodegradation. The study was performed at a JP-4 jet fuel-contaminated site at Eglin AFB, Florida. Site soils consisted of fine- to coarse-grained quartz sand with groundwater at a depth of 2 to 6 ft (0.61 to 1.8 m). Previous studies by Downey et al. (1988) and Hinchee et al. (1989) at the same site had shown that rapid decomposition of hydrogen peroxide occurred, even with the addition of phosphate as a peroxide stabilizer. In subsequent studies, hydrogen peroxide was injected at a concentration of 300 mg/L both with and without the addition of a phosphate-containing nutrient solution. As in previous studies, hydrogen peroxide decomposition was rapid, resulting in poor distribution of oxygen in groundwater. Addition of the phosphate-containing nutrient solution did not appear to improve hydrogen peroxide stability.

Other attempts have been made using hydrogen peroxide as an oxygen source. Although results indicate better hydrogen peroxide stability than achieved by Hinchee et al. (1989), it was

concluded that most of the hydrogen peroxide decomposed rapidly (Huling et al., 1990). Some degradation of aromatic hydrocarbons appears to have occurred; however, no change in total hydrocarbon contamination levels was detected in the soils (Ward, 1988).

In contrast to hydrogen peroxide use, when air is used as an oxygen source in unsaturated soil, 170 ft³ (4,800 L) of air must be delivered to provide the minimum oxygen required to degrade 1 lb (0.45 kg) of hydrocarbon (Table 2-1). Since costs associated with water-based delivery of oxygen can be relatively high, the use of gas-phase delivery results in a significant reduction in the cost associated with supplying oxygen¹.

An additional advantage of using a gas-phase process is that gases have greater diffusivity than liquids. At many sites, geologic heterogeneities cause fluid that is pumped through the formation to be channelled into the more-permeable pathways (e.g., in an alluvial soil with interbedded sand and clay, all of the fluid flow initially takes place in the sand). As a result, oxygen must be delivered to the less-permeable clay lenses through diffusion. In a gaseous system (as found in unsaturated soils), this diffusion can be expected to take place at rates at least three orders of magnitude greater than rates in a liquid system (as is found in saturated soils). Although it is not realistic to expect diffusion to aid significantly in water-based bioreclamation, diffusion of oxygen in a gas-phase system is a significant mechanism for oxygen delivery to less-permeable zones.

Given the advantages of using air rather than water as the oxygen source, several investigators began exploring the feasibility of an air-based oxygen supply system as a remedial option. A summary of the results of these investigations is presented in Section 2.2.

2.2 Bioventing Research and Development

Figure 2-1 provides a historical perspective of bioventing research and development. To the authors' knowledge, the first documented evidence of unsaturated zone biodegradation resulting from forced aeration was reported by the Texas Research Institute, Inc., in a 1980 study for the American Petroleum Institute. A large-scale model experiment was conducted to test the effectiveness of a surfactant treatment to enhance the recovery of spilled gasoline. The experiment accounted for only 8 gallons (30 L) of the 65 gallons (250 L) originally spilled and raised questions about the fate of the

¹ Refer to Section 5.0, Volume II for a comparison of costs associated with hydrogen peroxide use versus air (bioventing).

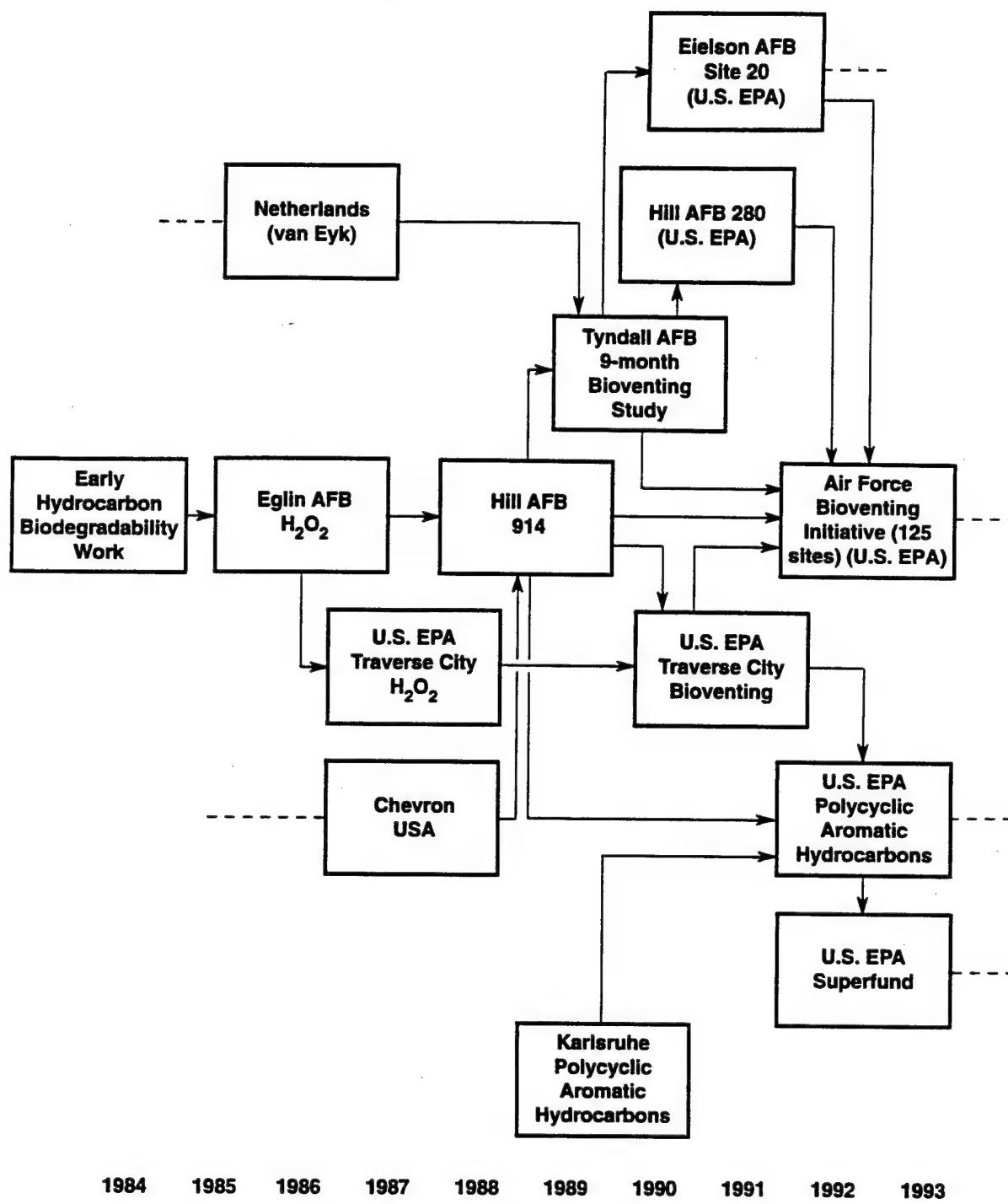


Figure 2-1. Historical Perspective of the Development of Bioventing

gasoline. Subsequently, a column study was conducted to determine a diffusion coefficient for soil venting. This column study evolved into a biodegradation study in which it was concluded that as much as 38% of the fuel hydrocarbons were biologically mineralized. Researchers concluded that venting not only would remove gasoline by physical means, but also would enhance microbial activity and promote biodegradation of the gasoline (Texas Research Institute, 1980; 1984).

To the authors' knowledge, the first actual field-scale bioventing experiments were conducted by Jack van Eyk for Shell Research. In 1982, at van Eyk's direction, the Shell Laboratory in Amsterdam, The Netherlands initiated a series of experiments to investigate the effectiveness of bioventing for treating hydrocarbon-contaminated soils. These studies were reported in a series of papers (Anonymous, 1986; Staatsuitgeverij, 1986; van Eyk and Vreeken, 1988; 1989a; and 1989b).

Wilson and Ward (1986) suggested that using air as a carrier for oxygen could be 1,000 times more efficient than using water, especially in deep, hard-to-flood unsaturated zones. They made the connection between oxygen supply via soil venting and biodegradation by observing that "soil venting uses the same principle to remove volatile components of the hydrocarbon." In a general overview of the soil venting process, Bennedsen et al. (1987) concluded that soil venting provides large quantities of oxygen to the unsaturated zone, possibly stimulating aerobic degradation. They suggested that water and nutrients also would be required for significant degradation and encouraged additional investigation into this area.

Biodegradation enhanced by soil venting has been observed at several field sites. Investigators claim that at a soil venting site for remediation of gasoline-contaminated soil, significant biodegradation occurred (measured by a temperature rise) when air was supplied. Investigators pumped pulses of air through a pile of excavated soil and observed a consistent rise in temperature, which they attributed to biodegradation. They claimed that the pile was cleaned up during the summer primarily by biodegradation (Conner, 1989). However, they did not control for natural volatilization from the aboveground pile, and not enough data were published to critically review their biodegradation claim.

Researchers at Traverse City, Michigan, observed a decrease in the toluene concentration in unsaturated zone soil gas, which they measured as an indicator of fuel contamination in the unsaturated zone. They assumed that advection had not occurred and attributed the toluene loss to biodegradation. The investigators concluded that because toluene concentrations decayed near the

oxygenated ground surface, soil venting is an attractive remediation alternative for biodegrading light volatile hydrocarbon spills (Ostendorf and Campbell, 1989).

The U.S. Air Force initiated its research and development program in bioventing in 1988 with a study at Site 914¹, Hill AFB, Utah. This site initially was operated as a soil vapor extraction unit, but was modified to a bioventing system after 9 months of operation because there was evidence of biodegradation and in an effort to reduce costs by reducing off-gas. Moisture and nutrient addition were studied at this site; however, while moisture addition appeared to improve biodegradation, nutrient addition did not. Final soil sampling demonstrated that benzene, toluene, ethylbenzene, and xylenes (BTEX) and total petroleum hydrocarbon (TPH) levels were reduced to below regulatory levels, and this site became the first Air Force site that was closed through in situ bioremediation. During this study, it became apparent that bioventing had great potential for remediating JP-4 jet fuel-contaminated soils. It also was apparent that additional research would be needed before the technology could be applied routinely in the field.

Following the Site 914, Hill AFB study, a more controlled bioventing study was completed at Tyndall AFB², Florida. This study was designed to monitor specific process variables and the subsequent effect on biodegradation of hydrocarbons. Several important findings resulted from this work, including the effect of air flowrates on removal by biodegradation and volatilization, the effect of temperature on biodegradation rates, the lack of microbial stimulation from the addition of moisture and nutrients, and the importance of natural nitrogen supply through nitrogen fixation. In addition, initial and final contaminant measurements showed over 90% removal of BTEX. Although this study was short-term, it illustrated the effectiveness of bioventing.

The studies conducted at Hill and Tyndall AFBs provided valuable information on bioventing. However, it was apparent that long-term, controlled bioventing studies were necessary to fully evaluate and optimize the technology. In 1991, long-term bioventing studies were initiated at Site 280, Hill AFB, Utah and at Site 20, Eielson AFB, Alaska³. These studies were joint efforts between the U.S. EPA and the U.S. Air Force Environics Directorate of the Armstrong Laboratory. These

¹ Refer to Section 4.1 for a detailed discussion of this study.

² Refer to Section 4.2 for a detailed discussion of this study.

³ Refer to Sections 4.3 and 4.4, respectively, for detailed discussions of these studies.

studies have involved intensive monitoring of several process variables, including the effect of soil temperature on biodegradation rates, surface emission analyses, and optimization of flowrate.

Based on the success of these previous studies, in 1992, AFCEE initiated the Bioventing Initiative where pilot-scale bioventing systems were installed at 125 contaminated sites located throughout the continental United States and in Hawaii, Alaska, and Johnston Atoll (Figure 2-2). The sites varied dramatically in climatic and geologic conditions. Contaminants typically were petroleum hydrocarbons from JP-4 jet fuel, heating oils, waste oils, gasoline, and/or diesel; however, some fire training areas also were studied where significant concentrations of solvents were present. This manual is a product of this study and represents the culmination of data collected from these sites and other projects.

In addition to these studies, other bioventing studies have been conducted by several researchers. A summary of some sites where bioventing has been applied is shown in Table 2-2¹. The scale of application and contaminant type is given, as well as the biodegradation rate, if known. The studies listed in Table 2-2 are limited to those where the study was conducted *in situ*, where no inoculum was added to site soils, and flowrates were optimized for biodegradation, not volatilization. It is important to distinguish between bioventing and SVE systems. Bioventing systems operate at flowrates optimized for biodegradation not volatilization, although some volatilization may occur. SVE systems operate at flowrates optimized for volatilization, although some biodegradation may occur. Therefore, flowrates and configuration of the two systems are significantly different.

The following section describes the basic structure for field studies conducted as part of the Bioventing Initiative. Data from these studies were used to generate this two-volume document.

¹ Only select Bioventing Initiative sites are included in this table. A presentation of data from all Bioventing Initiative sites is provided in Section 4.1.



Figure 2-2. Locations of Bioventing Initiative Sites

Table 2-2. Summary of Reported In Situ Respiration Rates and Bioventing Data

Site	Scale of Application	Contaminant	In Situ Respiration Rates (mg/kg-day unless marked)	Reference
Albemarle County, VA	Pilot scale	Acetone, toluene, benzene, naphthalene	1.5 – 26	Leeson et al., 1994
Eielson AFB, AK	Pilot scale	JP-4 jet fuel	0.82 – 8.2	Hinchee & Ong, 1992 Leeson et al., 1995 Sayles et al., 1994a
Fallon NAS, NE	In situ respiration test	JP-5 jet fuel	4.2	Hinchee et al., 1991b
Galena AFS, AK, Saddle Tank Farm	Pilot scale	Diesel	11 – 30	Ong et al., 1994
Hill AFB, Utah, Site 914	Full scale, 2 years	JP-4 jet fuel	up to 8.5	Hinchee et al., 1991a
Hill AFB, Utah, Site 280	Full scale	JP-4 jet fuel	0.27 (site average)	Battelle, 1994 Sayles et al., 1994b
Eglin AFB, FL	Full Scale	Gasoline	4.0	Downey et al., 1994
Kenai, Alaska, Site 1-33	Pilot scale	Crude oil, petroleum	2.7 – 25	Hinchee, unpublished data
Kenai, Alaska, Site 3-9	Pilot scale	Crude oil	0.64 – 12	Hinchee, unpublished data
Massachusetts	Full scale	Gasoline	Not measured	Brown & Crosbie, 1994
Minnesota	Full scale	Gasoline	15, 4.9, 3.1, 0.20	Newman et al., 1993
The Netherlands	Full scale	Gasoline	570 kg hydrocarbon removed during 2-yr study	van Eyk, 1994
The Netherlands	Undefined	Undefined	1.6 – 4.2	Urlings et al., 1990
The Netherlands	Field pilot, 1 year	Diesel	6.9	van Eyk & Vreeken, 1989b
Patuxent River NAS, MD	In situ respiration test	JP-5 jet fuel	2.6	Hinchee et al., 1991b

Table 2-2. Summary of Reported In Situ Respiration Rates and Bioventing Data (continued)

Site	Scale of Application	Contaminant	In Situ Respiration Rates (mg/kg-day unless marked)	Reference
Prudhoe Bay	Pilot scale	Diesel	8.6 – 11	Ong et al., 1994
St. Louis Park, MN, Reilly Tar Site	Pilot scale	PAH	0.55 – 2.2 mg PAH/kg-day	Alleman et al., 1995
Seattle, WA	Full Scale	Diesel	6.0	Baker et al., 1993
Southern CA	Full scale	Gasoline, hydraulic oil	0.14	Zachary & Everett, 1993
Tinker AFB, OK	In situ respiration test	JP-4 and mixed fuels	2.3 – 15	Hinchee & Smith, 1991
Tyndall AFB, FL	Field pilot, 1 year and in situ respiration test	JP-4 jet fuel	1.6 – 16	Miller, 1990 Hinchee et al., 1991b
Undefined	Full scale	Gasoline and diesel	50 kg/(well day)	Ely & Heffner, 1988
Undefined	Full scale	Diesel	100 kg/(well day)	Ely & Heffner, 1988
Undefined	Full scale	Fuel oil	60 kg/(well day)	Ely & Heffner, 1988
Valdez, Site A	Pilot scale	Crude oil	8.7 – 16.0	Foor and Hinchee, 1993

2.3 Structure of Bioventing Initiative Field Treatability Studies and Bioventing System Design

The design of the field treatability studies and final bioventing system was developed based on experience at previous studies at Hill, Tyndall, and Eielson AFBs. The *Test Plan and Technical Protocol for a Treatability Test for Bioventing* (Hinchee et al., 1992) was written to standardize all field methods from treatability tests to well installations. The document allowed for collection of consistent data from 125 sites, which provided a strong database for evaluating bioventing potential. At all sites, the following activities were conducted:

- site characterization, including a small-scale soil gas survey and collection of initial soil and soil gas samples for analysis of BTEX, TPH, and soil physicochemical characteristics;
- field treatability studies, including an in situ respiration test and a soil gas permeability test;
- identification of a background, uncontaminated area for comparison with the contaminated area of background respiration rates and nutrient levels;
- installation of a blower for 1-year of operation (typically configured for air injection), if results of field treatability studies were positive;
- conduct of 6-month and 1-year in situ respiration tests at sites where a blower had been installed; and
- collection of final soil and soil gas samples for analyses of BTEX and TPH.

Of particular significance were the use of the in situ respiration test to measure microbial activity and the use of air injection instead of extraction for air delivery.

The in situ respiration test was developed to rapidly measure aerobic biodegradation rates in situ at discrete locations¹. Biodegradation rates calculated from the in situ respiration test are useful (1) for assessing the potential application of bioremediation at a given site, (2) for estimating the time required for remediation at a given site, and (3) for providing a measurement tool for evaluating the effects of various environmental parameters on microbial activity and ultimately on bioventing

¹ Refer to Section 1.4, Volume II for methods for conducting the in situ respiration test and analyses of test data.

performance. The actual effect of individual parameters on microbial activity is difficult to assess in the field due to interference and interactions among these parameters. The *in situ* respiration test integrates all factors to simply assess whether the microorganisms are metabolizing the fuel. Data from the *in situ* respiration test and site measurements were used to conduct a statistical analysis of the observed effects of the site measurements on microbial activity in the field. The statistical analysis was constructed to account for parameter interactions. These results are discussed in detail in Section 5.0.

Also of note is that 120 of the 125 bioventing systems installed were configured for air injection. Prior to the bioventing studies conducted at Hill (Site 280) and Eielson AFBs, bioventing systems typically were operated in the extraction configuration, similar to SVE systems. However, research at Hill and Eielson AFBs demonstrated that air injection is a feasible and more efficient alternative to air extraction, resulting in a greater proportion of hydrocarbon biodegradation rather than volatilization and reduced air emissions¹. Therefore, the air injection configuration was selected for the basic bioventing system at Bioventing Initiative sites.

The results generated from the Bioventing Initiative are summarized in detail in Section 5.0 and are used to illustrate the basic principles of bioventing and microbial processes discussed in Section 3.0. The design guidelines presented in this manual have culminated primarily from the experience of installing and operating the 125 Bioventing Initiative sites. These design guidelines represent the basic bioventing system, which is applicable to the majority of sites suitable for bioventing. The following section addresses emerging techniques for modifications to the basic bioventing system described in this document for sites that are not amenable to standard bioventing methods.

2.4 Emerging Techniques for Modifications to Bioventing Systems

Several techniques are being investigated as a means of modifying the conventional bioventing system described in this document. These techniques have not been tested extensively in the field; therefore, their potential feasibility is unknown. They are briefly presented in this section to illustrate their potential application.

¹ Refer to Section 2.1, Volume II for a discussion of air injection versus extraction.

The bioventing modifications being investigated are designed to address specific challenges in bioventing:

- Injection of pure oxygen instead of air for treatment of low-permeability soils. Because only low flowrates are possible in low-permeability soils, injection of pure oxygen may be useful for providing larger oxygen concentrations for a given volume than is possible with air injection.
- Soil warming for bioventing in cold climates. Soil warming can be used to increase biodegradation rates, thus decreasing remediation times. This technique has been studied in detail at Site 20, Eielson AFB, Alaska¹, but would be an option only in extreme environments.
- Remediation of recalcitrant compounds through ozonation. Ozonation may be used to partially oxidize more recalcitrant contaminants, making them more susceptible to biodegradation. This technique would not be necessary at petroleum-contaminated sites, but may be considered at sites contaminated with compounds such as polycyclic aromatic hydrocarbons (PAHs) or pesticides.
- Remediation of contaminated saturated soils through air sparging. Air sparging is being investigated as a means of aerating saturated soil to enhance biodegradation, as well as volatilization. However, studies to date have been inconclusive concerning its effectiveness due to a lack of adequate controls and measurement techniques.

The techniques described above represent potential future areas of investigation in the bioremediation field. The following chapters describe the principles of bioventing, which also apply to the techniques described in this section.

¹ Refer to Section 4.4 for a discussion of this site and the cost benefits of soil warming.

3.0 PRINCIPLES OF BIOVENTING

In this chapter, basic principles fundamental to the bioventing process are discussed to provide a clear understanding of the many physical, chemical, and biological processes that impact the ultimate feasibility of bioventing. Recognizing the significance of these different processes will lead to more efficient bioventing design and operation. Specific topics to be considered in this chapter include:

- soil gas permeability, contaminant diffusion and distribution, and zone of oxygen influence (Section 3.1);
- subsurface distribution of an immiscible liquid (Section 3.1);
- environmental factors which affect microbial processes, such as electron acceptor conditions, moisture content, pH, temperature, nutrient supply, contaminant concentration, and bioavailability (Section 3.2);
- compounds targeted for removal through bioventing (Section 3.3); and
- BTEX versus TPH removal during petroleum bioventing (Section 3.4).

3.1 Physical Processes Affecting Bioventing

Four primary physical characteristics affect bioventing. These include soil gas permeability, contaminant diffusion in soil, contaminant distribution, and zone of oxygen influence. Each of these parameters is discussed in the following sections.

3.1.1 Soil Gas Permeability

Assuming contaminants are present that are amenable to bioventing, geology probably is the most important site characteristic for a successful bioventing application. Soils must be sufficiently permeable to allow movement of enough soil gas to provide adequate oxygen for biodegradation, on the order of 0.25 to 0.5 pore volumes per day.

Soil gas permeability is a function of both soil structure and particle size, as well as of soil moisture content. Typically, permeability in excess of 0.1 darcy is adequate for sufficient air

exchange. Below this level, bioventing certainly is possible, but field testing may be required to establish feasibility.

When the soil gas permeability falls below approximately 0.01 darcy, soil gas flow is primarily through either secondary porosity (such as fractures) or through any more permeable strata that may be present (such as thin sand lenses). Therefore, the feasibility of bioventing in low-permeability soils is a function of the distribution of flow paths and diffusion of air to and from the flow paths within the contaminated area.

In a soil that is of a reasonable permeability, a minimum separation of 2 to 4 ft (0.61 to 1.2 m) between vertical and horizontal flow paths and contaminant may still result in successful treatment due to oxygen diffusion. However, the degree of treatment will be very site-specific.

Bioventing has been successful in some low-permeability soils, such as a silty clay site at Fallon Naval Air Station (NAS), Nevada (Kittel et al., 1995), a clayey site at Beale AFB, California (Phelps et al., 1995), a silty site at Eielson AFB, Alaska (Leeson et al., 1995), and a silty clay site in Albemarle County, Virginia (Leeson et al., 1994), and at many Bioventing Initiative sites. Grain size analysis was conducted on several samples from each site in the Bioventing Initiative. The relative distribution of fine-grained soils is illustrated in Figure 3-1. Sufficient soil gas permeability has been demonstrated at many sites with silt and clay contents exceeding 80% by weight. Approximately 50% of the sites tested contained greater than 50% clay and silt fractions. Oxygen distribution has generally been adequate in soils where permeability values exceeded 0.1 darcy, with oxygen detected at ambient levels in all nine of the monitoring points installed. Few sites had permeability less than 0.1 darcy; therefore, data for analysis are limited. The greatest limitation to bioventing at Bioventing Initiative sites has been excessive soil moisture. A combination of high soil moisture content and fine-grained soils has made bioventing impractical at only three of the 125 test sites.

In general, our calculated soil gas permeability values have exceeded suggested literature values reported in Johnson et al. (1990) for silt and clay soils. This is likely due to the heterogeneous nature of most soils, which contain lenses of more permeable material or fractures which aid in air distribution.

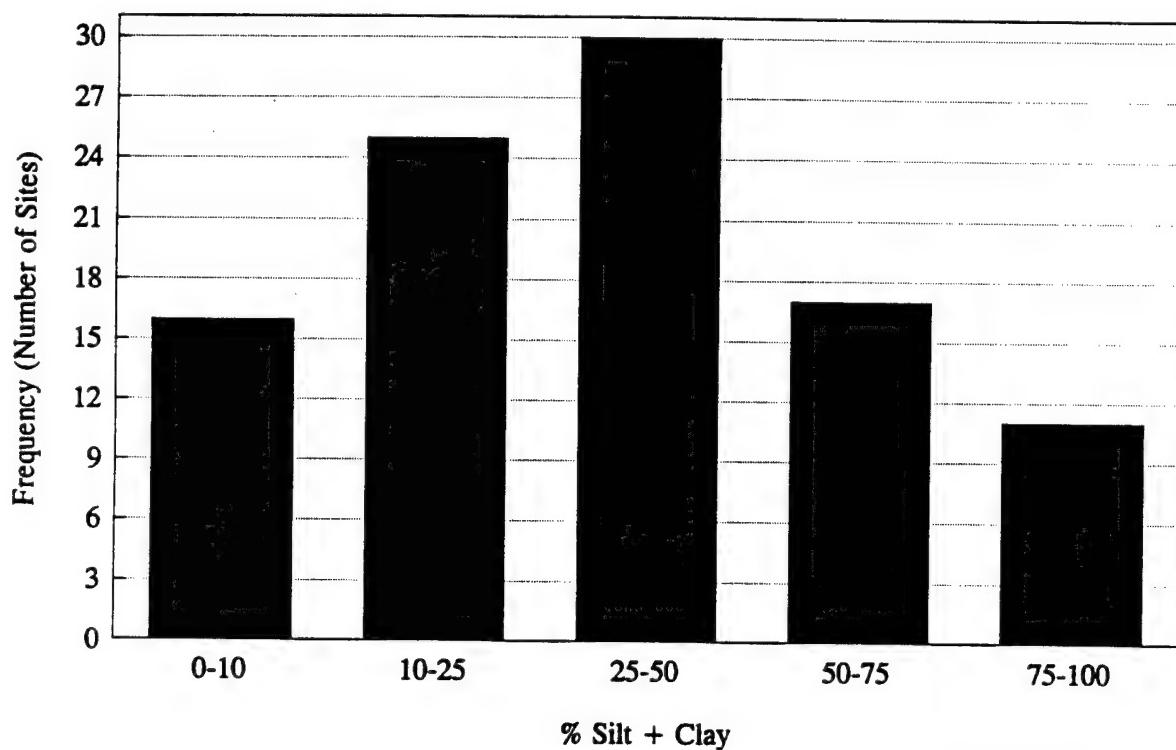


Figure 3-1. Distribution of Silt- and Clay-Sized Particles at Bioventing Initiative Sites

3.1.2 Contaminant Distribution

Another important factor affecting the feasibility of bioventing is the contaminant distribution throughout the site. Because bioventing is in essence an air delivery system designed to efficiently provide sufficient oxygen to contaminated soils, it is important to have a clear understanding of subsurface contaminant distribution. Many of the sites at which bioventing can be applied are contaminated with immiscible liquids, such as petroleum hydrocarbons. When a fuel release occurs, the contaminants may be present in any or all of four phases in the geologic media:

- sorbed to the soils in the vadose zone;
- in the vapor phase in the vadose zone;
- in free-phase form floating on the water table or as residual saturation in the vadose zone; and/or
- in the aqueous phase dissolved in pore water in the vadose zone or dissolved in the groundwater.

Of the four phases, dissolved petroleum contaminants in the groundwater frequently are considered to be of greatest concern due to the risk of humans being exposed to contaminants through drinking water. However, the free-phase and sorbed-phase hydrocarbons act as feedstocks for groundwater contamination, so any remedial technology aimed at reducing groundwater contamination must address these sources of contamination. Also, hydrocarbons in the vadose zone can produce a volatile organic carbon (VOC) threat in subsurface buildings or structures.

Immiscible liquids are classified as less dense, nonaqueous-phase liquids (LNAPLs) if their density is less than water or dense, nonaqueous-phase liquids (DNAPLs) if their density is greater than water. In general, most petroleum hydrocarbons, such as gasoline, are LNAPLs, whereas most chlorinated solvents, such as trichloroethylene (TCE), are DNAPLs. Due to these differences in densities, subsurface spills of LNAPLs and DNAPLs will behave differently at a given site, with LNAPLs distributed primarily in the vadose zone and DNAPLs distributed in both the unsaturated and saturated zone. Given that bioventing is primarily a vadose zone treatment process, this discussion will focus on the behavior of LNAPLs.

When a large enough fuel spill occurs, the fuel is retained within approximately 10 to 20% of the pore volume of the soil and eventually may come to rest on the water table. Contaminants then partition among the various phases existing within the subsurface environment. Fluids can move through the subsurface via various mechanisms, such as advection and diffusion. LNAPLs are likely to migrate through the vadose zone relatively uniformly until the capillary fringe is reached. The LNAPL will then spread laterally along the saturated zone. Water table fluctuation may result in LNAPL below the water table; however, an LNAPL will not permeate the water-saturated zone unless a critical capillary pressure is exceeded, which is a function of the porous medium pore sizes.

In the vadose zone, components of the LNAPL may partition into the vapor phase or the aqueous phase (pore water), sorb onto solids, or remain in the free product. Contaminants in free product may partition into the vapor phase, depending on their vapor pressures at the temperature and pressure existing in the vadose zone. Once in the vapor phase, these contaminants can migrate in response to advection and diffusion. Raoult's law is used to describe partitioning at equilibrium between an immiscible phase and a vapor phase:

$$C_v = \chi C_{vsat} \quad (3-1)$$

where: C_v = volumetric concentration of the contaminant (x) in the vapor phase (g_x/L_{vapor});

χ = mole fraction of the contaminant (dimensionless); and

C_{vsat} = saturated vapor concentration of the contaminant (g_x/L_{vapor}).

C_{vsat} is further defined as:

$$C_{vsat} = \frac{(MW_x) P_v}{R T_{abs}} \quad (3-2)$$

where: MW_x = molecular weight of the contaminant (g_x/mole_x);

P_v = vapor pressure of pure contaminant at temperature T (atm);

R = gas constant ($L\text{-atm}/\text{mole}\cdot^{\circ}\text{K}$); and

T_{abs} = absolute temperature ($^{\circ}\text{K}$).

Free product in contact with groundwater may leach contaminants into the groundwater or contaminants may dissolve into pore water in the vadose zone, depending on the solubility of specific components. Once in the groundwater, contaminants can migrate through the subsurface in response to a gradient in the aqueous-phase total potential (i.e., advection) or by a difference in the aqueous-phase chemical concentrations. The equilibrium relationship between the aqueous and the immiscible phases is described as:

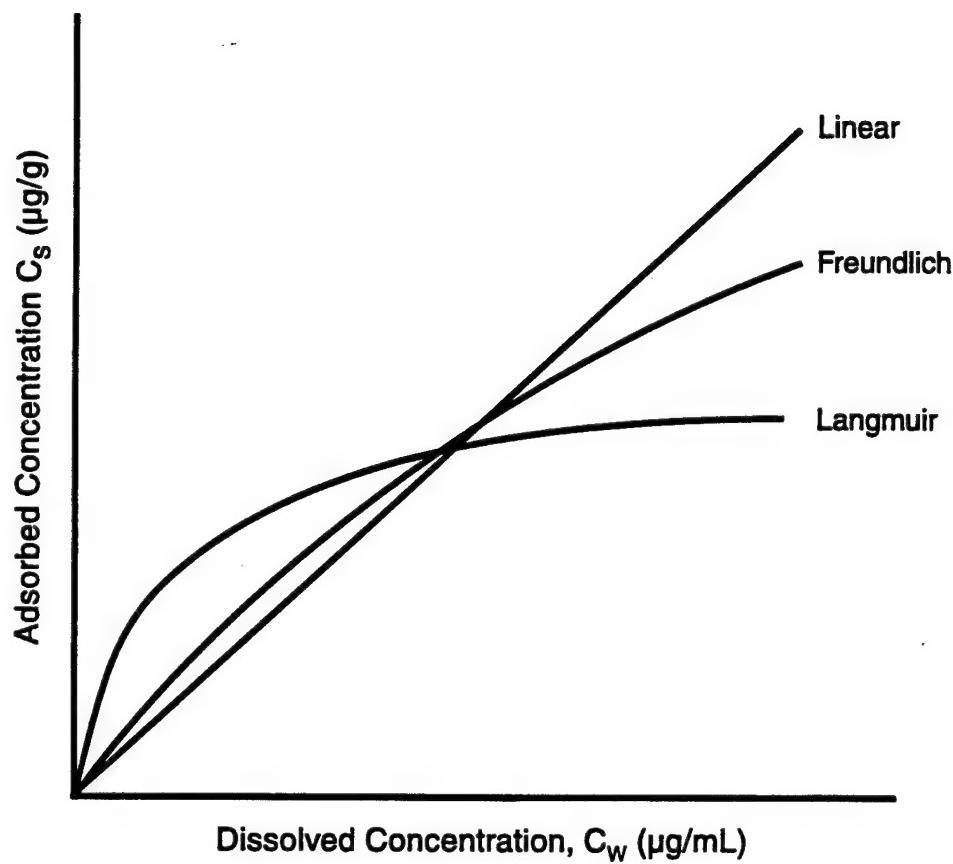
$$C_w = \chi s_x \quad (3-3)$$

where: C_w = volumetric concentration of contaminant x in the aqueous phase ($\text{g}_x/\text{L}_{\text{aqueous}}$);

s_x = solubility of pure contaminant x in water ($\text{g}_x/\text{L}_{\text{water}}$).

Sorption of contaminants is a complex process involving several different phenomena including coulomb forces, London-van der Waals forces, hydrogen bonding, ligand exchange, dipole-dipole forces, dipole-induced dipole forces, and hydrophobic forces (Wiedemeier et al., 1995). In the case of hydrocarbons, due to their nonpolar nature, sorption most often occurs through hydrophobic bonding to organic matter. Hydrophobic bonding often is a dominant factor influencing the fate of organic chemicals in the subsurface (DeVinny et al., 1990). The degree of sorption generally is empirically related by the organic content of the soil and by the octanol-water partition coefficient of a particular compound.

Sorption isotherms generally follow one of three shapes: Langmuir, Freundlich, or linear (Figure 3-2). The Langmuir isotherm describes the sorbed contaminant concentration as increasing linearly with concentration then leveling off as the number of sites available for sorption are filled. This isotherm accurately describes the situation at or near the contaminant source where concentrations are high. The Freundlich isotherm assumes an infinite number of sorption sites, which would accurately describe an area some distance from the contaminant source where concentrations are dilute. The mathematical expression contains a chemical-specific coefficient that may alter the linearity of the isotherm. The linear isotherm is relatively simple and is valid for dissolved



CD1.Lesson\36-10

Figure 3-2. Sorption Isotherms

compounds at less than one-half of their solubility (Lyman et al., 1992). This isotherm is typically valid to describe hydrocarbon sorption.

The linear isotherm is expressed mathematically as:

$$C_s = K_d C_w \quad (3-4)$$

where: C_s = quantity of contaminant x sorbed to the solid matrix (g_x/g_{soil});

K_d = sorption coefficient ($L_{aqueous}/g_{soil}$).

The sorption coefficient may be determined experimentally, estimated based on values published in the literature, or estimated using the octanol/water partition coefficient (K_{ow}) and the organic carbon fraction (f_{oc}) of the soil. The sorption coefficient can be estimated using the following mathematical expression:

$$K_d = K_{ow} f_{oc} \quad (3-5)$$

Some values for K_{ow} are provided in Table 3-1.

In practice, at equilibrium, the concentration of most petroleum hydrocarbon compounds of interest in the aqueous or vapor phases is driven by the immiscible phase, if present, and the sorbed phase, if the immiscible phase is not present. If no immiscible phase is present, and all sorption sites on the solid soil matrix are not occupied¹, the vapor or aqueous phase concentration is a function of the sorbed concentration. This relationship is illustrated in Figure 3-3.

This relationship typically follows a Langmuir type curve. If the concentration in the soil is in excess of the sorption capacity of the soil², the aqueous-phase and vapor-phase concentrations are Raoult's law-driven and are independent of the hydrocarbon concentration in the soil. This is an important concept in attempting to interpret soil gas or groundwater data. For example, in a sandy

¹ In most soils, this is probably at a concentration of less than 100 to 1,000 mg/kg.

² In most soils, this is probably at a concentration greater than 100 to 1,000 mg/kg.

Table 3-1. Values for Key Properties of Select Petroleum Hydrocarbons

Compound	K _{ow}	Solubility (mg/L)	Vapor Pressure (mm Hg) ¹
Benzene	131.82	1,750 ²	75
Ethylbenzene	1,349	152 ²	10 ^{79°F}
Heptane		50	40
Hexane		20	150
Toluene	489.9	537 ³	20 ^{65°F}
<i>o</i> -xylene	891	152 ²	7
<i>m</i> -xylene	1,585	158 ²	9
<i>p</i> -xylene	1,513.6	198 ²	9

¹ Vapor pressure at 68°F unless noted.² Calculated at 20°C.³ Calculated at 20°C.

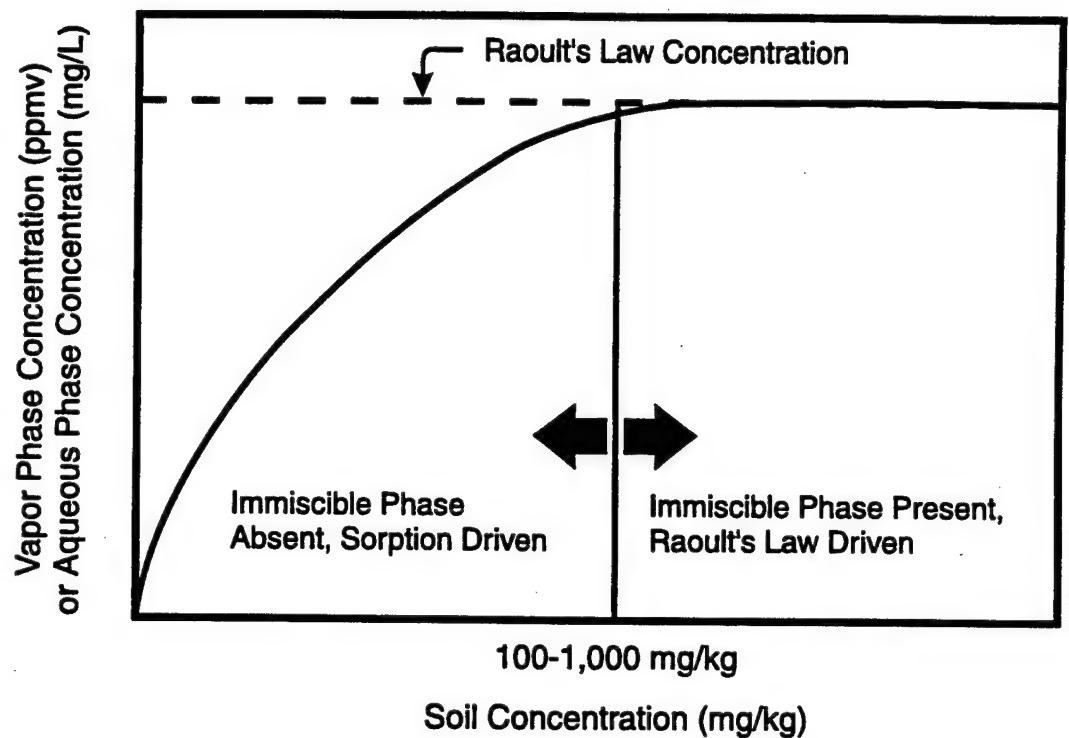


Figure 3-3. Relationship Between Sorbed Contaminant Concentration and Vapor- or Aqueous-Phase Concentrations

site at which free product has been detected, the highest soil hydrocarbon concentrations may exceed 25,000 mg/kg. Yet 99% remediation to 250 mg/kg may not affect the equilibrium soil gas or groundwater hydrocarbon concentrations.

In terms of contaminant distribution, difficulties in applying bioventing arise when significant quantities of the contaminant are in the capillary fringe or below the water table due to groundwater fluctuations. Treatment of the capillary fringe is possible and screening of venting wells below the water table is recommended to ensure treatment of this area¹. However, the ability of bioventing to aerate the capillary fringe and underlying water table has not been evaluated. Limited oxygenation is anticipated due to water-filled pore space. If significant contamination exists below the water table, dewatering should be considered as a means of exposing any contaminated soil to injected air. Alternatively, a combination of air sparging and bioventing may provide more efficient air delivery to the capillary fringe; however, air sparging has not been well-documented and many parameters are still unknown concerning its applicability and effectiveness.

3.1.3 Oxygen Radius of Influence

An estimate of the oxygen radius of influence (R_i) of venting wells is an important element of a full-scale bioventing design. This measurement is used to design full-scale systems, specifically to space venting wells, to size blower equipment, and to ensure that the entire site receives a supply of oxygen-rich air to sustain in situ biodegradation.

The radius of oxygen influence is defined as the radius to which oxygen has to be supplied to sustain maximal biodegradation. This definition of radius of influence is different than is typically used for SVE, where radius of influence is defined as the maximum distance from the air extraction or injection well where vacuum or pressure (soil gas movement) occurs. The oxygen radius of influence is a function of both air flowrates and oxygen utilization rates, and therefore depends on site geology, well design, and microbial activity.

The radius of influence is a function of soil properties, but also is dependent on the configuration of the venting well, extraction or injection flowrates, and microbial activity, and it is altered by soil stratification. In soils with less-permeable lenses adjacent to more-permeable soils,

¹ Refer to Section 2.5, Volume II for a discussion of vent well construction.

injection into the permeable layer will produce a greater radius of influence than could be achieved in homogeneous soils. On sites with shallow contamination, the radius of influence also may be increased by impermeable surface barriers such as asphalt or concrete. Frequently, however, paved surfaces do not act as vapor barriers. Without a tight seal to the native soil surface¹, the pavement will not significantly impact soil gas flow.

Microbial activity will impact the oxygen radius of influence. As microbial activity increases, the effective treated area will decrease. Therefore, it is desirable to estimate the oxygen radius of influence at times of peak microbial activity and to design the bioventing system based on these measurements.

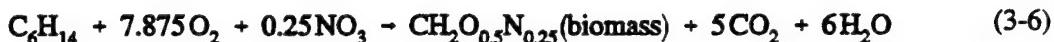
3.2 Microbial Processes Affecting Bioventing

Biological treatment approaches rely on organisms to destroy or reduce the toxicity of contaminants. The advantages of chemical and physical treatment approaches generally are outweighed by the ability of microorganisms to mineralize contaminants, thereby eliminating the process of transferring contaminants from one medium (i.e., soil and soil vapor) into another (i.e., activated carbon) that will still require treatment. In addition, through microbial processes, it is possible to treat large areas relatively inexpensively and with relatively noninvasive techniques. This section discusses kinetics of microbial metabolism and environmental parameters which affect the microbial processes bioventing is dependent upon, thereby potentially affecting the efficacy of bioventing.

3.2.1 Microbial Kinetics

In biological processes, microorganisms degrade organic compounds either directly to obtain carbon and/or energy, or fortuitously in a cometabolic process with no significant benefit to the microorganism. As an example, a stoichiometric equation describing degradation of *n*-hexane is shown:

¹ It is the authors' experience that at most sites, this seal does not occur.



In the case of bioventing, where microorganisms are stimulated *in situ*, the microorganisms are at equilibrium, and little net biomass growth occurs. In other words, biomass decay approximately balances biomass growth. Consequently, where no net biomass is produced, Equation (3-6) will reduce to:



Based on Equation (3-7), 9.5 moles of oxygen are required for every mole of hydrocarbon consumed, or, on a weight basis, approximately 3.5 g of oxygen are required for every 1 g of hydrocarbon consumed.

To predict the amount of time required to bioremediate a site, it is necessary to understand the microbial kinetics of substrate (contaminant) utilization. Most substrate utilization falls under the heading of primary substrate utilization, in which growth on a carbon source supplies most of the carbon and energy for the microorganism. In cases where a contaminant does not supply the primary source or cannot be used for carbon and energy, secondary substrate utilization or cometabolism may occur. During the bioventing process, primary substrate utilization generally describes the kinetics of the reactions taking place; however, in some instances, cometabolic processes also may occur. For example, at sites contaminated with both fuels and solvents such as TCE, cometabolic bioventing may account for degradation of TCE.

Primary substrate utilization has been described through an empirical approach by the Monod expression:

$$-\frac{dS}{dt} = \frac{kXS}{K_s + S} \quad (3-8)$$

where: S = concentration of the primary substrate (contaminant) (g_S/L);
 t = time (minutes);
 k = maximum rate of substrate utilization ($\text{g}_S/\text{g}_X\text{-min}$);
 X = concentration of microorganisms (g_X/L); and

K_S = Monod half-velocity constant (g_S/L).

At high substrate concentrations ($S > > K_S$), the rate of substrate utilization is at a maximum, limited by some other factor such as oxygen, nutrients, or the characteristics of the microorganism. In this instance, the rate of substrate utilization will be first-order with respect to cell density, but zero-order with respect to substrate concentration. Conversely, when the primary substrate concentration is very low ($S < < K_S$), the substrate utilization rate will be first-order with respect to both cell density and substrate concentration. In a well-designed bioventing system, kinetics based on oxygen utilization are zero-order. However, the rate based on petroleum or other contaminant removal may be described by Monod or inhibition kinetics.

Monod kinetics have been widely applied to conventional wastewater treatment where the compounds being treated generally are bioavailable and readily degradable. Bioventing typically is applied to aerobically biodegradable compounds; however, the maximum rate of biodegradation (k) is much lower than for most wastes in conventional wastewater treatment. For example, Howard et al. (1991) estimated that benzene has an aerobic half-life (dissolved in groundwater) of 10 days to 24 months, whereas ethanol (a compound more typical of conventional wastewater treatment) is estimated to have a half-life of 0.5 to 2.2 days. Bioventing kinetics are further complicated by bioavailability of the contaminants, driven at least in part by solubilization. Since microorganisms exist in pore water, contaminants must partition into the pore water to be available to be degraded. Although high soil contaminant concentrations may be present, the actual concentration of hydrocarbon dissolved in the pore water and available to the microorganisms may be low.

In practice, oxygen utilization rates tend to decline slowly with time during remediation. At many sites, this trend may be difficult to follow over periods of less than 1 to 3 years because of other variables affecting the rate, such as temperature and soil moisture. This decline may not be indicative of true first-order kinetics, but simply may be the result of selective early removal of more degradable compounds such as benzene.

3.2.2 Environmental Parameters Affecting Microbial Processes

Bioventing is dependent upon providing microorganisms optimal conditions for active growth. Several factors may affect a microorganism's ability to degrade contaminants, including:

- availability and type of electron acceptors;
- moisture content;
- soil pH;
- soil temperature;
- nutrient availability; and
- contaminant concentration.

Each of these parameters was measured at Bioventing Initiative sites. The actual effect of individual parameters on microbial activity is difficult to assess in the field due to interference and interactions among these parameters. The *in situ* respiration test was used as a measurement tool that integrates all factors to assess whether the microorganisms are metabolizing the fuel. Data from the *in situ* respiration test and site measurements were used to conduct a statistical analyses of the observed effects of the site measurements on microbial activity in the field. The statistical analysis was constructed to account for parameter interactions. These results are discussed in detail in Section 5.0. A more general discussion of the significance of each of these parameters and its affect on microbial activity is provided in Sections 3.3.2.1 through 3.3.2.7.

3.2.2.1 Electron Acceptor Conditions

One of the most important factors which influences the biodegradability of a compound is the type and availability of electron acceptors. For example, following a hydrocarbon spill, as a result of the hydrocarbon biodegradability, anaerobic conditions typically predominate in the subsurface because of oxygen depletion from microbial activity. While hydrocarbons may undergo limited biodegradation under anaerobic conditions (Bilbo et al., 1992; Mormile et al., 1994), in general, aerobic conditions are most suitable for relatively rapid remediation of petroleum hydrocarbons. Therefore, oxygen supply is critical to the success of a bioventing system. In field studies, oxygen has been found to be the most important factor in determining the success of a bioventing system (Hinchee et al., 1989; Miller et al., 1991). This has been confirmed by the Bioventing Initiative. At these sites, oxygen has been found to the primary factor limiting microbial activity at all but three sites (Miller et al., 1993).

3.2.2.2 Moisture Content

Soil moisture content may impact the bioventing process by its affect on microorganisms or soil gas permeability. Microorganisms require moisture for metabolic processes and for solubilization of energy and nutrient supplies. Conversely, soil moisture content directly affects the soil permeability, with high moisture contents resulting in poor distribution of oxygen. In practice, soil moisture has been found to directly limit biodegradation rates only where bioventing has been implemented in very dry desert environments. A more common influence of moisture is that excess moisture has led to significant reductions in soil gas permeability. One of the major objectives of the Bioventing Initiative was to assess the effects of moisture on biodegradation.

The range of soil moisture content measured at Bioventing Initiative sites is shown in Figure 3-4. The lowest soil moisture content measured was 2% by weight, and microbial activity still was observed in these soils. Figure 3-5 illustrates the observed relationship between soil moisture and oxygen utilization rates. To date, a strong correlation has not been recorded between moisture content and oxygen utilization rate, although a slight positive relationship has been observed¹.

At a desert site at the Marine Corps Air Ground Combat Center, Twentynine Palms, California, soil moisture content appeared to detrimentally affect microbial activity. Soil moisture content ranged from 2% to 4% by weight and, although the site was contaminated with jet fuel, significant oxygen limitation was not observed. An irrigation system was installed at the site in an effort to enhance microbial activity. The site was irrigated for 1 week, then bioventing was initiated for 1 month before conducting an in situ respiration test. In situ respiration rates measured after irrigation were significantly higher than those measured prior to irrigation (Figure 3-6). In addition, prior to irrigation, oxygen was not consumed below approximately 17% before microbial activity stopped. After irrigation, activity continued until oxygen was completely consumed to less than 1%. These results demonstrated that, in extreme cases, moisture addition may improve the performance of bioventing systems through enhanced microbial activity.

It may be assumed that air injection bioventing will dry out the soil to a point what would be detrimental to microbial growth, necessitating humidification of the injection air. However, a simple calculation as shown in Example 3-1 illustrates that over a 3-year period, moisture loss is minimal.

¹ Refer to Section 5.2 for a discussion of the statistical relationship between moisture content and oxygen utilization rates.

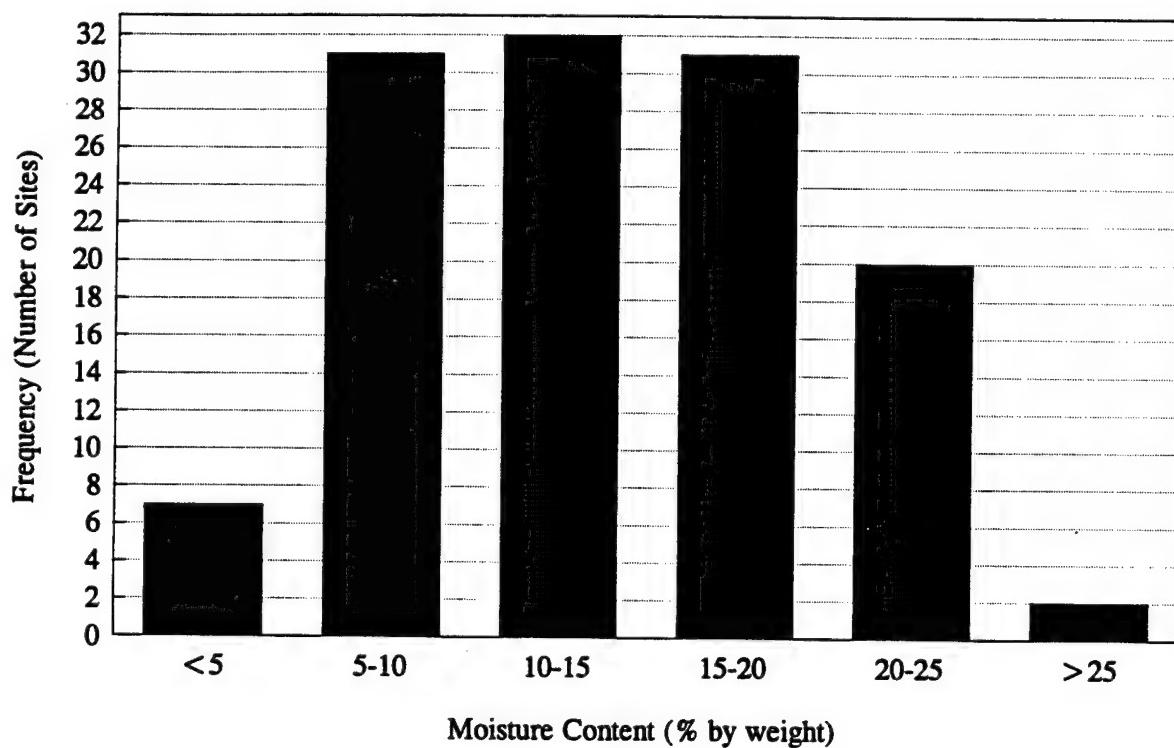


Figure 3-4. Soil Moisture Content Measurements at Bioventing Initiative Sites

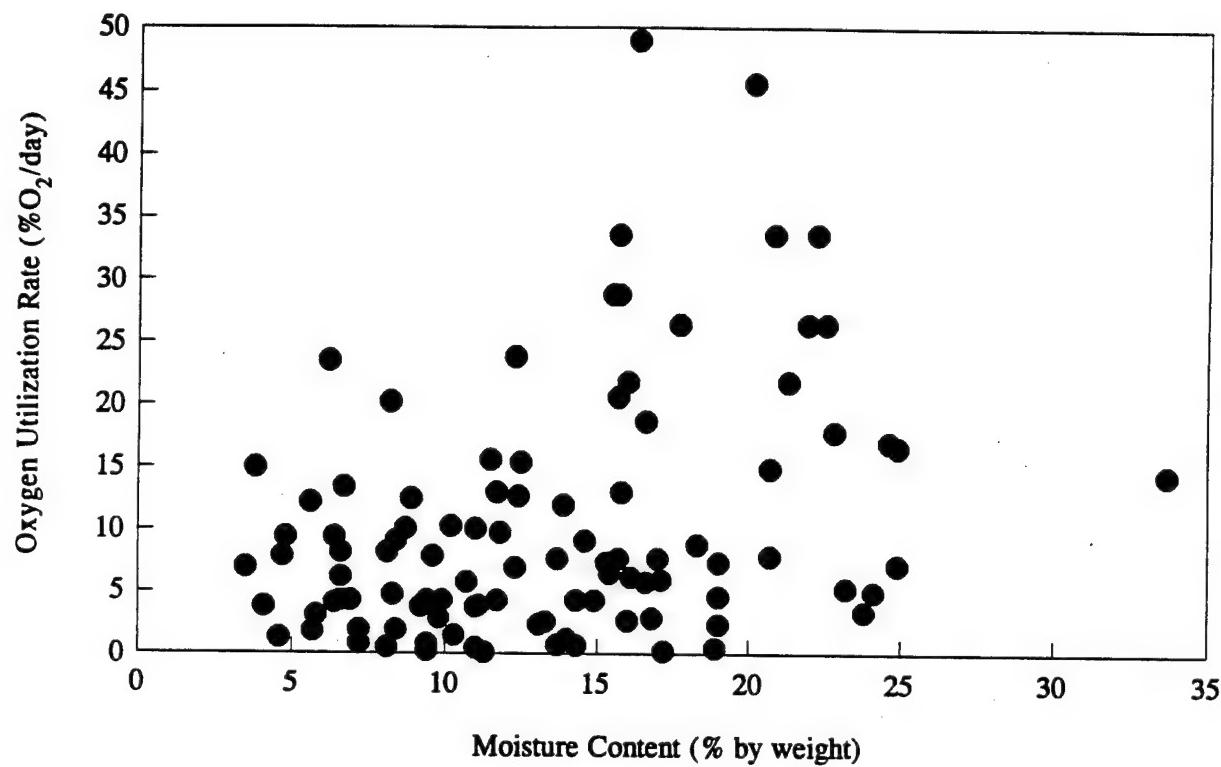


Figure 3-5. Direct Correlation Between Oxygen Utilization Rates and Soil Moisture Content at Bioventing Initiative Sites

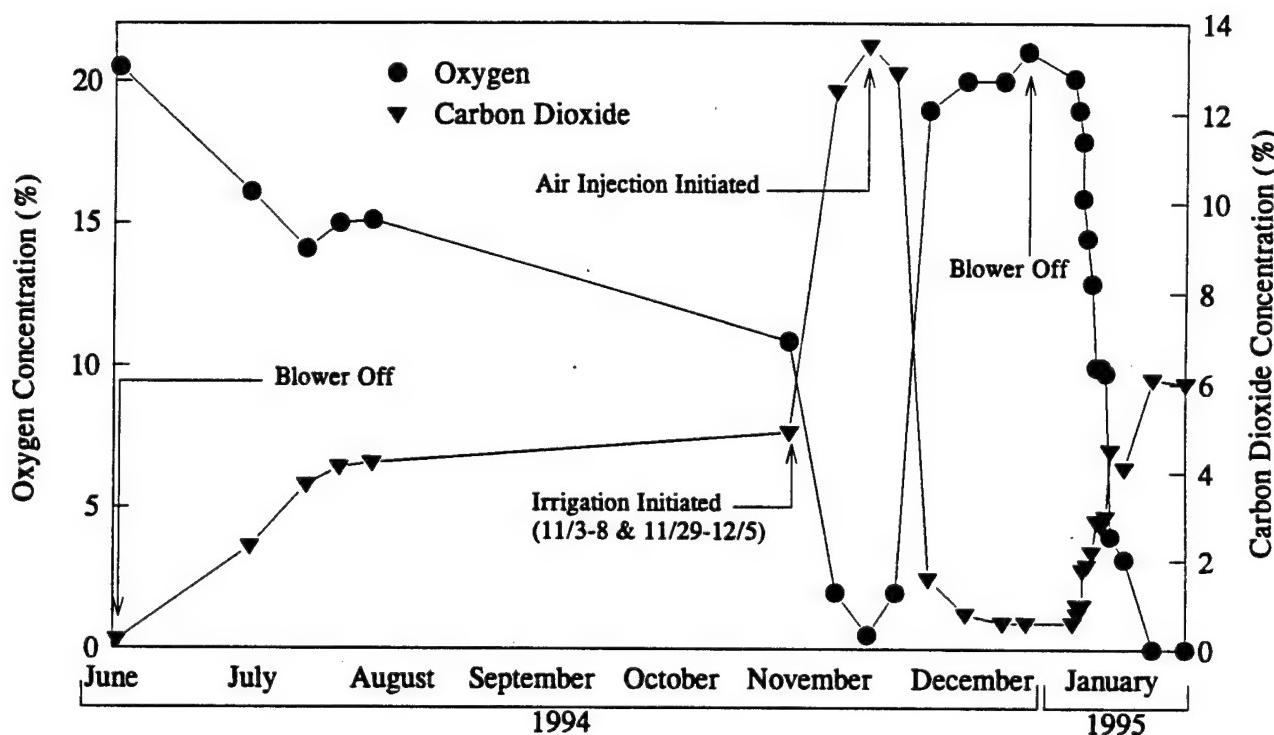


Figure 3-6. Oxygen and Carbon Dioxide Concentrations Prior to and After Irrigation at Twentynine Palms, California

Drying and moisture loss as a result of bioventing usually are a problem only very near the vent well or if very high air injection rates are used (typically not the case in properly designed bioventing systems). Sites typically have several moisture sources that also make drying due to air injection negligible, such as rain and snow, and water as a byproduct of mineralization (generated at a rate of 1.5 kg water for every 1 kg of hydrocarbon degraded¹).

Example 3-1. Moisture Content Change During Air Injection and Water Generated During Biodegradation: For this test:

Vapor pressure (P_{water})	=	17.5 mm Hg
Flowrate (Q)	=	1 pore volume/day, typical of bioventing
Volume of treatment area (V)	=	12,300 m ³
Biodegradation rate (k_B)	=	3 mg/kg-day
Initial moisture content	=	15% by weight
Soil bulk density	=	1,440 kg/m ³
Assume worst case of 0% humidity and no infiltration.		

To calculate the total water at the site initially, the mass of soil is first calculated:

$$12,300 \text{ m}^3 \times \frac{1,440 \text{ kg}}{\text{m}^3} = 1.8 \times 10^7 \text{ kg soil}$$

Therefore, the initial mass of water is:

$$(1.8 \times 10^7 \text{ kg soil}) \times 0.15 = 2.7 \times 10^6 \text{ kg H}_2\text{O}$$

Since the flowrate is equivalent to one pore volume/day, the mass of water removed per day will be equal to the mass of water in the vapor phase of the treated area, which can be calculated using the Ideal Gas law:

$$\frac{\text{Moles H}_2\text{O removed}}{\text{day}} = \frac{P_{\text{water}} V}{RT} = \frac{17.5 \text{ mmHg} \times 12,300 \text{ m}^3}{\left(0.0623 \frac{\text{m}^3 \cdot \text{mmHg}}{\text{mole} \cdot ^\circ\text{K}}\right) \times 298^\circ\text{K}}$$

¹ Refer to Equation (3-7) for the stoichiometry of this calculation.

$$\frac{\text{Moles H}_2\text{O removed}}{\text{day}} = 11,600 = 210 \frac{\text{kg}}{\text{day}}$$

Total water removal in 3 years:

$$210 \frac{\text{kg}}{\text{day}} \times 1,095 \text{ days} = 230,000 \text{ kg removed}$$

This water loss represents a fairly small percentage, or:

$$\frac{230,000 \text{ kg evaporated}}{2.7 \times 10^6 \text{ initial mass}} = 0.086 \approx 8.6\% \text{ H}_2\text{O loss}$$

This is equivalent to a soil moisture drop from approximately 15% to 13.7%. Assuming a contaminated thickness of 10 ft (3 m), an infiltration rate of approximately 2.4 inches (6.1 cm) in 3 years, or less than 1 inch (2.5 cm) per year, would replace the lost moisture. In practice, some drying very close to the vent well may be observed, but usually is not.

Water loss also will be replaced through biodegradation of hydrocarbons. Calculating the total mass of hydrocarbons degraded over 3 years:

$$3 \frac{\text{mg}}{\text{kg-day}} \times 1,095 \text{ days} \times (1.8 \times 10^7 \text{ kg soil}) \times \frac{\text{kg}}{10^6 \text{ mg}} = 59,000 \text{ kg hydrocarbon degraded}$$

Based on the stoichiometry in Equation (2-1), 1.5 kg of water are generated for every kg of hydrocarbon degraded, the amount of water generated would be:

$$59,000 \text{ kg hydrocarbon} \times \frac{1.5 \text{ kg water}}{\text{kg hydrocarbon}} = 88,500 \text{ kg water}$$

Therefore, total water removal in three years must also account for the water generation, where:

$$230,000 \text{ kg} - 88,500 \text{ kg H}_2\text{O} = 141,500 \text{ kg H}_2\text{O loss}$$

This is equivalent to a water loss of 5.3% over 3 years.

3.2.2.3 Soil pH

Soil pH also may affect the bioremediation process, since microorganisms require a specific pH range in order to survive. Most bacteria function best in a pH range between 5 and 9 with the optimum being slightly above 7 (Dragun, 1988). A shift in pH may result in a shift in the makeup of the microbial population, because each species will exhibit optimal growth at a specific pH. Throughout the Bioventing Initiative, pH has not been found to limit in situ bioremediation, and is probably only of concern where contamination has radically altered the existing pH.

Figure 3-7 illustrates the range of soil pH found at the Bioventing Initiative sites to date. In general, the majority of sites have fallen within the "optimal" pH range for microbial activity of 5 to 9. However, microbial respiration based on oxygen utilization has been observed at all sites, even in soils where the pH was below 5 or above 9. Figure 3-8 illustrates the observed relationship between pH and oxygen utilization rates. Based upon these observations, it appears that pH is not a concern when bioventing at most sites¹.

3.2.2.4 Soil Temperature

Soil temperature may significantly affect the bioremediation process. Microbial activity has been reported at temperatures varying from -12 to 100°C (10 to 212°F) (Brock et al., 1984); however, the optimal range for biodegradation of most contaminants is generally much narrower. An individual microorganism may tolerate a temperature peak of up to approximately 40°C (104°F). However, a microorganism's optimal growth temperature will vary depending on climate. For example, microorganisms in a subarctic environment may exhibit optimal growth at 10°C (50°F), whereas microorganisms in a subtropical environment may exhibit optimal growth at 30°C (86°F).

It has generally been observed that biodegradation rates double for every 10°C (50°F) temperature increase, up to some inhibitory temperature. The van't Hoff-Arrhenius equation expresses this relationship quantitatively as:

¹ Refer to Section 5.2 for a discussion of the statistical relationship between pH and oxygen utilization rates.

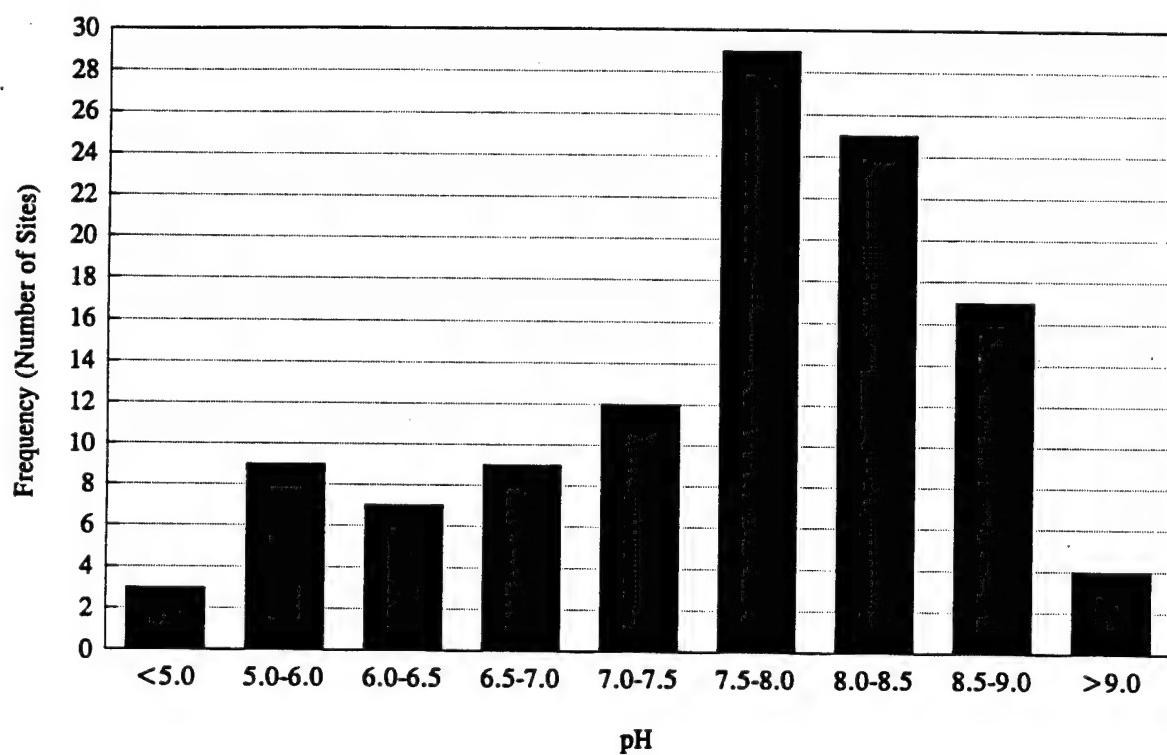


Figure 3-7. Soil pH Measurements at Bioventing Initiative Sites

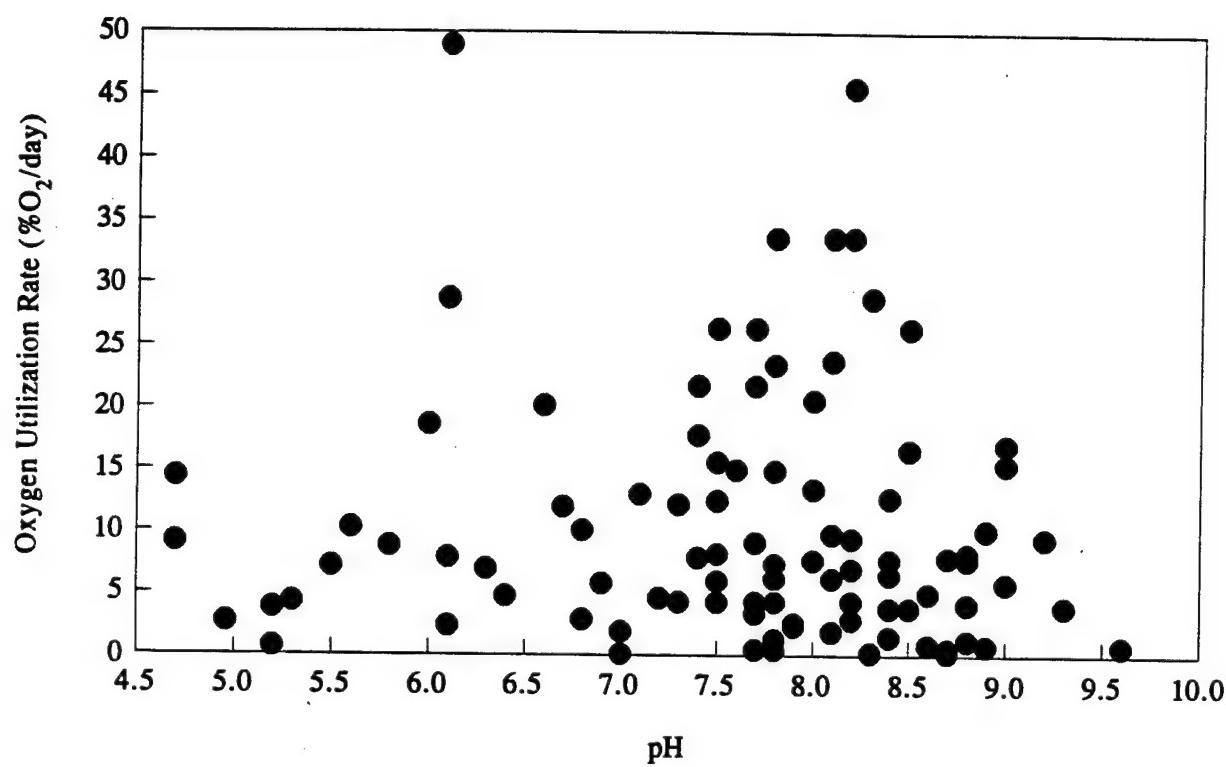


Figure 3-8. Correlation Between Oxygen Utilization Rate and Soil pH at Bioventing Initiative Sites

$$k_T = k_o e^{\frac{-E_a}{RT}} \quad (3-9)$$

where: k_T = temperature-corrected biodegradation rate (% O₂/day)

k_o = baseline biodegradation rate (% O₂/day)

E_a = activation energy (cal/mole)

R = gas constant (1.987 cal/°K-mol)

T_{abs} = absolute temperature (°K)

Miller (1990) found E_a equal to 8 to 13 kcal/mole for in situ biodegradation of jet fuel. In the 17 to 27°C (63 to 81°F) range, the van't Hoff-Arrhenius relationship accurately predicted biodegradation rates. A similar analysis was conducted at Site 20, Eielson AFB, Alaska, where the activation energy was found to be equal to 13.4 kcal/mole (Example 3-2). Figure 3-9 illustrates the relationship between oxygen utilization rate and temperature observed at Site 20, Eielson AFB, a JP-4 jet fuel-contaminated site.

Example 3-2. Calculation of the van't Hoff-Arrhenius Constant From Site Data:

Various forms of soil warming were tested at Site 20, Eielson AFB, Alaska. This resulted in a wide range of temperatures and biodegradation rates measured at the same site.

In order to calculate the van't Hoff-Arrhenius constant, the log of the biodegradation rate must be calculated versus the inverse of the temperature to provide the relationship:

$$\ln \left(\frac{k_T}{k_o} \right) = \frac{-E_a}{R} \times \frac{1}{T} \quad (3-10)$$

The slope of the linear regression of inverse temperature versus oxygen utilization rate is -6740°K (Figure 3-9). Therefore,

$$\frac{E_a}{R} = -6740$$

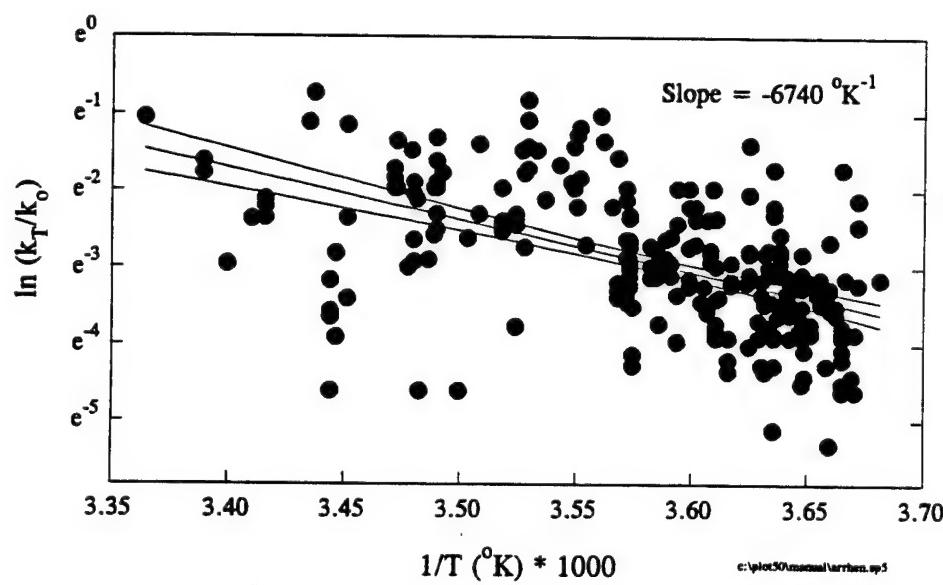
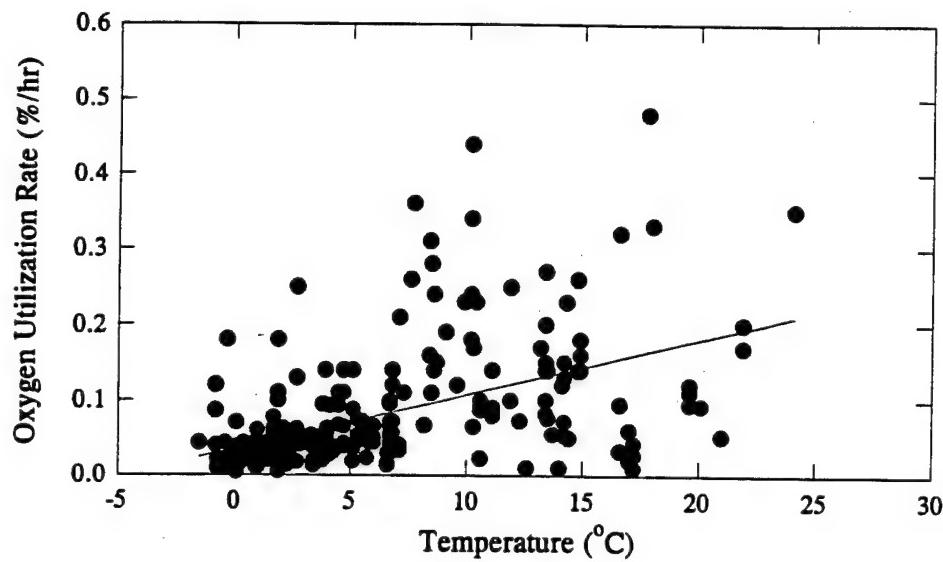


Figure 3-9. Soil Temperature Versus Biodegradation Rate at Site 20, Eielson AFB, Alaska

$$\frac{E_a}{1.987 \frac{\text{cal}}{\text{°K} \cdot \text{mole}}} = - 6740$$

$$E_a = 1.987 \frac{\text{cal}}{\text{°K} \cdot \text{mole}} \times - 6740 = 13,390 \frac{\text{cal}}{\text{mole}} \approx 13.4 \frac{\text{kcal}}{\text{mole}}$$

Heat addition may improve bioventing processes. Solar warming, warm water infiltration, and buried heat tape have been used to increase soil temperature. Their use has resulted in increased microbial activity and contaminant degradation (Leeson et al., 1995). Selection of a soil warming technique will depend on cost considerations versus remediation time requirements¹. While warm water infiltration or heat tape can significantly increase biodegradation rates, the cost is significantly higher than simply using surface insulation or no heating method. The use of warm water infiltration, although effective, is limited to very permeable soils, to ensure that adequate drainage of the applied water will occur. The use of soil heating to increase biodegradation rates may prove cost effective only in cold regions, such as Alaska.

3.2.2.5 Nutrient Supply

In order to sustain microbial growth, certain nutrients must be available at minimum levels. The following nutrients/cofactors are known to be required in order to support microbial growth: calcium, cobalt, copper, iron, magnesium, manganese, molybdenum, nitrogen, phosphorus, potassium, sodium, sulfur, and zinc. Nitrogen and phosphorus are required in the greatest concentrations and are the nutrients most likely to be limiting. The remaining chemicals are considered micronutrients, because they are required in only small quantities and generally are available in excess in nature.

Nutrients are required as components of the microbial biomass. The need for these nutrients is very different from the need for oxygen (or other electron donors) and the carbon source.

¹ Refer to Section 4.4 for a discussion of the cost benefit of soil warming.

Nutrients are not destroyed, but are recycled by the ecosystem. Thus, like oxygen, a steady input of nutrients is not required.

An approach to estimation of nutrient requirements, suggested by John T. Wilson of the U.S. EPA Ada Laboratory, can be made based on microbial kinetics. Starting with:

$$\frac{dX}{dt} = k_B Y - k_d X \quad (3-11)$$

where: X = biomass (mg biomass/kg soil)

k_B = biodegradation rate (mg hydrocarbon/kg soil-day)

Y = cell yield (mg biomass/mg hydrocarbon)

k_d = endogenous respiration rate (day⁻¹)

Assuming that the biomass concentration achieves steady state during bioventing,

$$\frac{dX}{dt} = 0 = k_B Y - k_d X \quad (3-12)$$

Solving:

$$X = \frac{k_B Y}{k_d} \quad (3-13)$$

Little is known about the in situ cell yields or endogenous respiration rates of hydrocarbon-degrading organisms, but these parameters can be estimated based on ranges reported in the wastewater treatment literature (Metcalf and Eddy, 1979). An example for calculating required nutrients is shown in Example 3-3.

Example 3-3. Estimation of Nutrient Requirements In Situ: For a given site, the following is assumed:

$$\begin{aligned} k_B &= 10 \text{ mg/kg-day (typical rate found at bioventing sites)} \\ Y &= 0.5 \text{ mg/mg} \end{aligned}$$

$$k_d = 0.05/\text{day}$$

Solving:

$$X = \frac{10 \frac{\text{mg}}{\text{kg-day}} \times 0.5 \frac{\text{mg}}{\text{mg}}}{\frac{0.05}{\text{day}}} = 100 \frac{\text{mg}}{\text{kg}}$$

To sustain 100 mg/kg of biomass, the nutrient requirements may be estimated from biomass to nutrient ratios. A variety of ratios are found in the literature. For this example, a 100:10:1 ratio of biomass:nitrogen:phosphorus is assumed. This ratio yields a nutrient requirement of 10 mg/kg of nitrogen and 1 mg/kg of phosphorus. Thus, if the above assumptions hold, a site with at least these levels of nitrogen and phosphorus initially should not be rate-limited by nitrogen and phosphorus.

Most soils naturally contain nutrients in excess of the concentrations calculated in Example 3-3. Therefore, although the addition of nutrients may be desirable in hopes of increasing biodegradation rates, field research to date does not indicate the need for these additions (Dupont et al., 1991; Miller et al., 1991). Therefore, although nutrients are often added to bioremediation projects in anticipation of increased biodegradation rates, field data to date do not show a clear relationship between increased rates and supplied nutrients.

Concentrations of total Kjeldahl nitrogen (TKN) and total phosphorus at the Bioventing Initiative sites and the corresponding relationship between oxygen utilization rates are shown in Figures 3-10 through 3-13. Although optimal ratios of carbon, nitrogen, and phosphorus were not available at all sites, the natural nutrient levels were sufficient to sustain some level of biological respiration at all sites when the most limiting element, oxygen, was provided.

In controlled nutrient additions at Tyndall and Hill AFBs¹, no apparent increase in microbial activity was observed. Therefore, there appeared to be no benefit of nutrient addition. The relationship between oxygen utilization rates and TKN and total phosphorus are shown in Figures 3-11 and 3-13, respectively. As is illustrated in these figures, there is no correlation between phosphorus and oxygen utilization rates and only a weak relationship between TKN concentrations

¹ Refer to Sections 4.1 and 4.2 for detailed discussions of these sites.

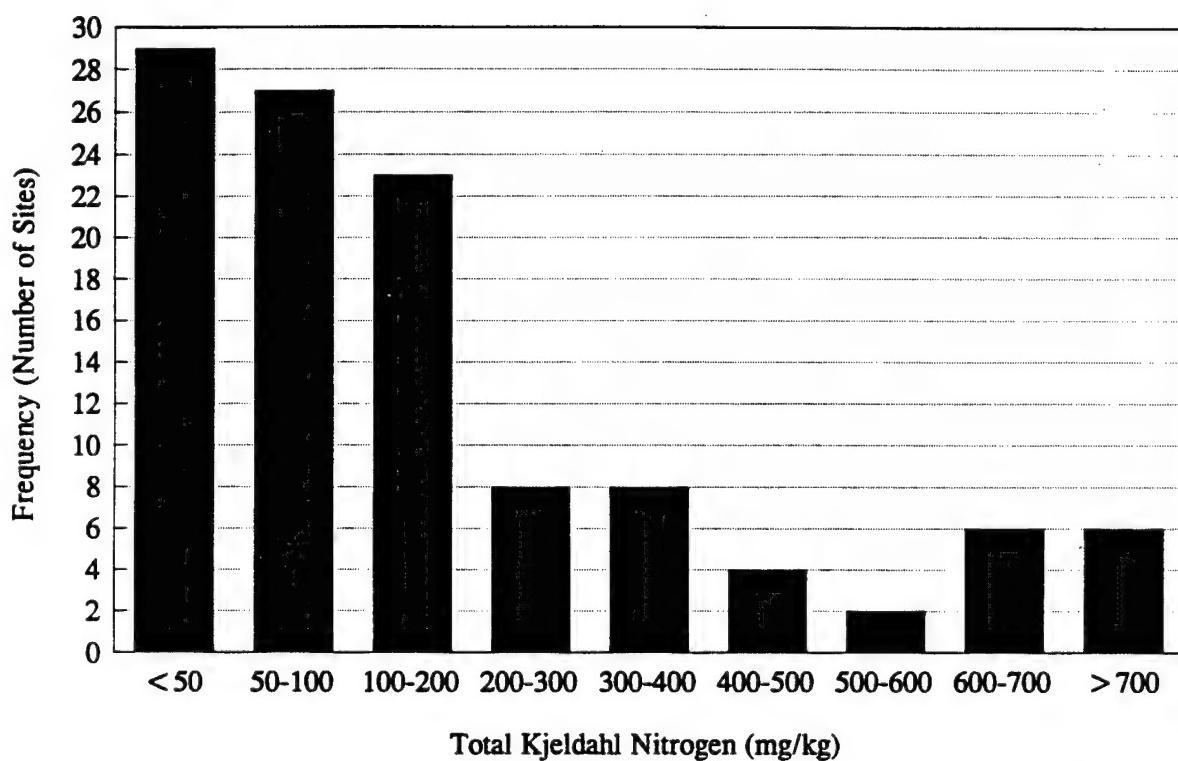
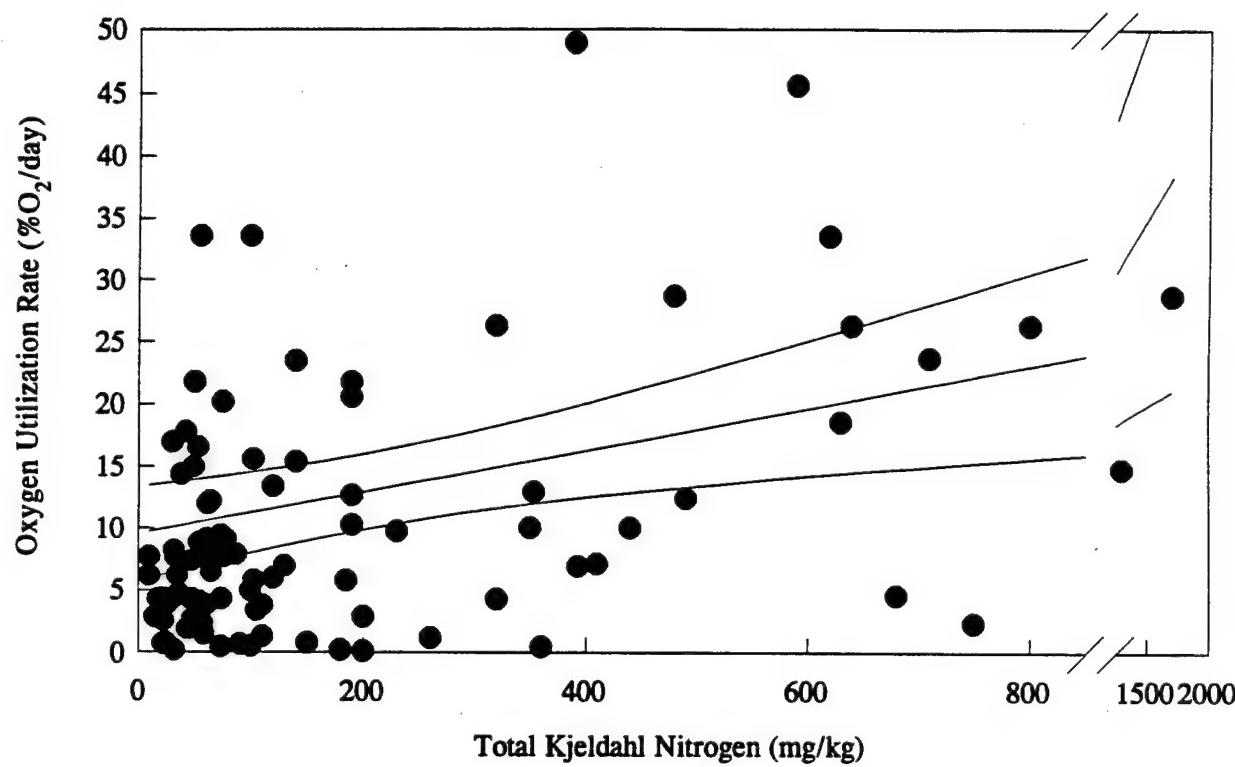


Figure 3-10. TKN Measurements at Bioventing Initiative Sites



c:\plot\90\manual\waterwtrk.sp5

Figure 3-11. Correlation Between Oxygen Utilization Rate and TKN at Bioventing Initiative Sites

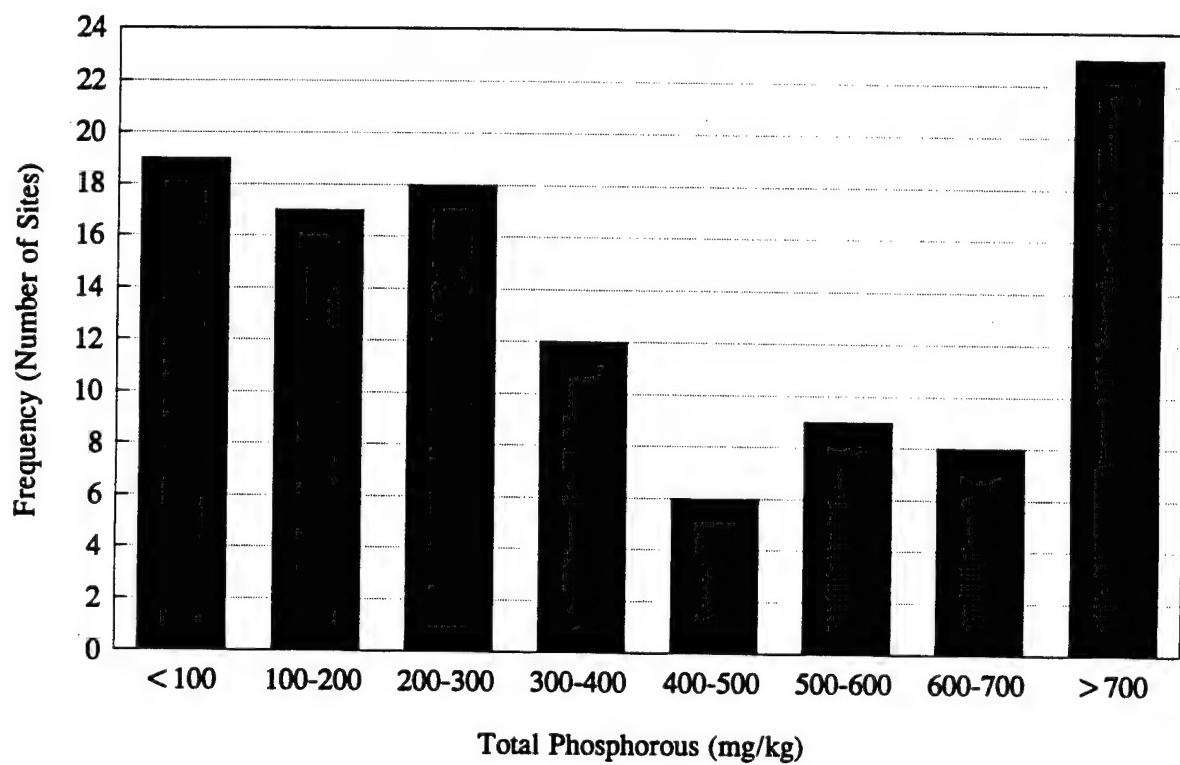


Figure 3-12. Total Phosphorus Measurements at Bioventing Initiative Sites

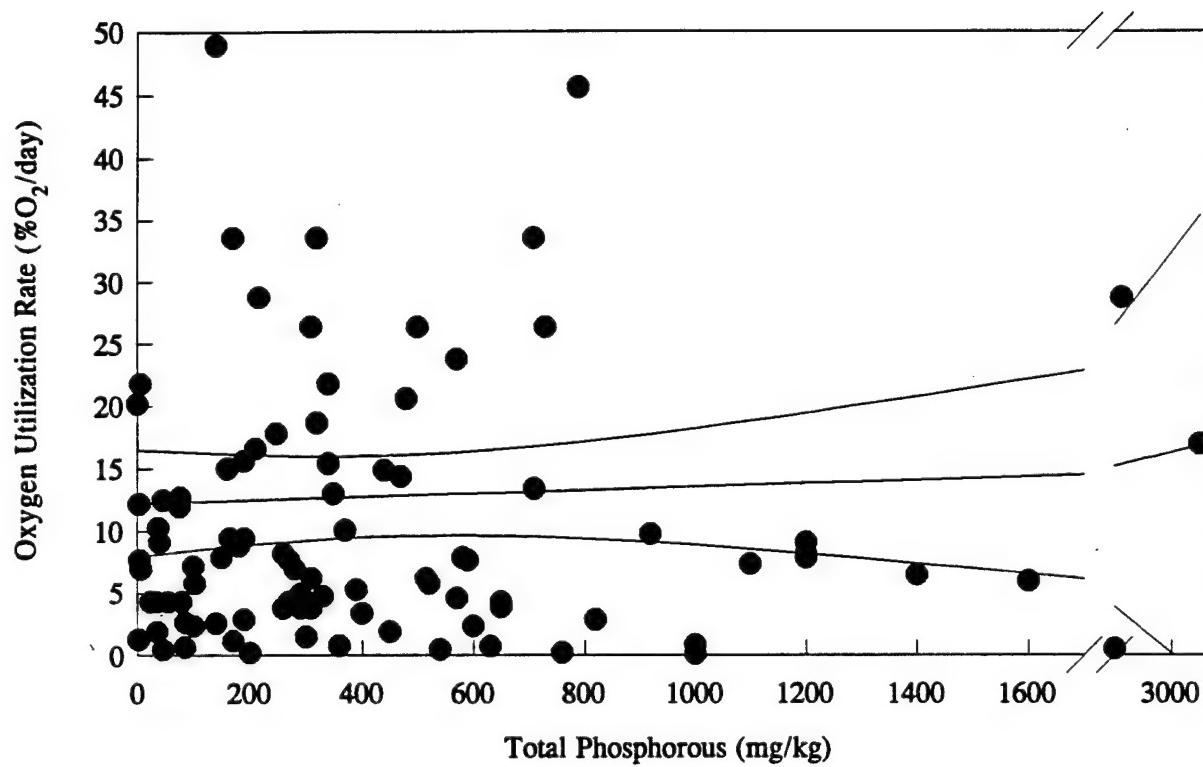


Figure 3-13. Correlation Between Oxygen Utilization Rate and Total Phosphorus at Bioventing Initiative Sites

and oxygen utilization rates, again emphasizing that natural ambient nutrient levels seem sufficient for microbial activity¹.

Figure 3-14 illustrates the range of iron concentrations measured at Bioventing Initiative sites. Iron concentrations varied greatly, with concentrations from less than 100 mg/kg to greater than 75,000 mg/kg. Soils in Hawaii and Alaska exhibited the highest iron contents. Although iron is a nutrient required for microbial growth, iron also may react with oxygen to form iron oxides. Theoretically, if a significant amount of iron oxidation occurs, the observed oxygen utilization rate² would not reflect microbial activity only. Therefore, calculated biodegradation rates would be an overestimate of actual biodegradation rates. Thus, background wells in uncontaminated areas are recommended in bioventing applications in areas of high iron concentrations. To date, this study has shown no correlation between iron content and oxygen utilization rates (Figure 3-15).

3.2.2.6 Contaminant Concentration

Contaminant concentration also may affect biodegradation of the contaminant itself. Excessive quantities of a contaminant can result in a reduction in biodegradation rate due to a toxicity effect. Conversely, very low concentrations of a contaminant also may reduce overall degradation rates because contact between the contaminant and the microorganism is limited and the substrate concentration is likely below S_{min} .

In practice, petroleum hydrocarbons in fuel mixtures do not generally appear to be toxic to the bioventing process. Other more soluble (i.e., phenolics) or less biodegradable compounds (i.e., TCE) may exhibit a toxicity effect and it has been reported that pure benzene may be toxic. Although a general relationship between bioventing rates and concentration no doubt exists, the relationship is complex and not fully understood. At sites where NAPLs are present (soil concentrations above the 100 to 1,000 mg/kg range), the bioavailable hydrocarbon is most probably limited by solubilization, which is linked to Raoult's law and, to an extent, is independent of total hydrocarbon concentration. Certainly, the NAPL distribution can affect the proportion of the soil in a site in which biodegradation

¹ Refer to Section 5.2 for a discussion of the statistical relationship between nutrients and oxygen utilization rates.

² As measured by in situ soil gas oxygen concentrations.

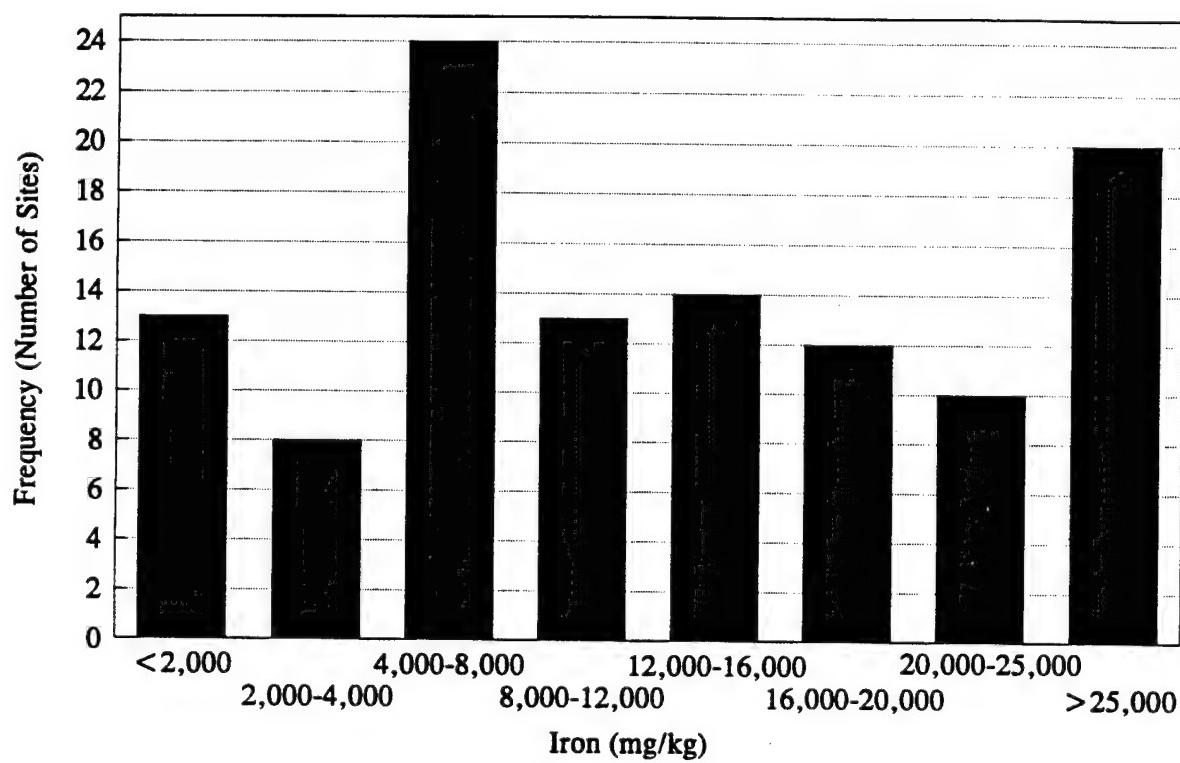


Figure 3-14. Iron Concentration Measurements at Bioventing Initiative Sites

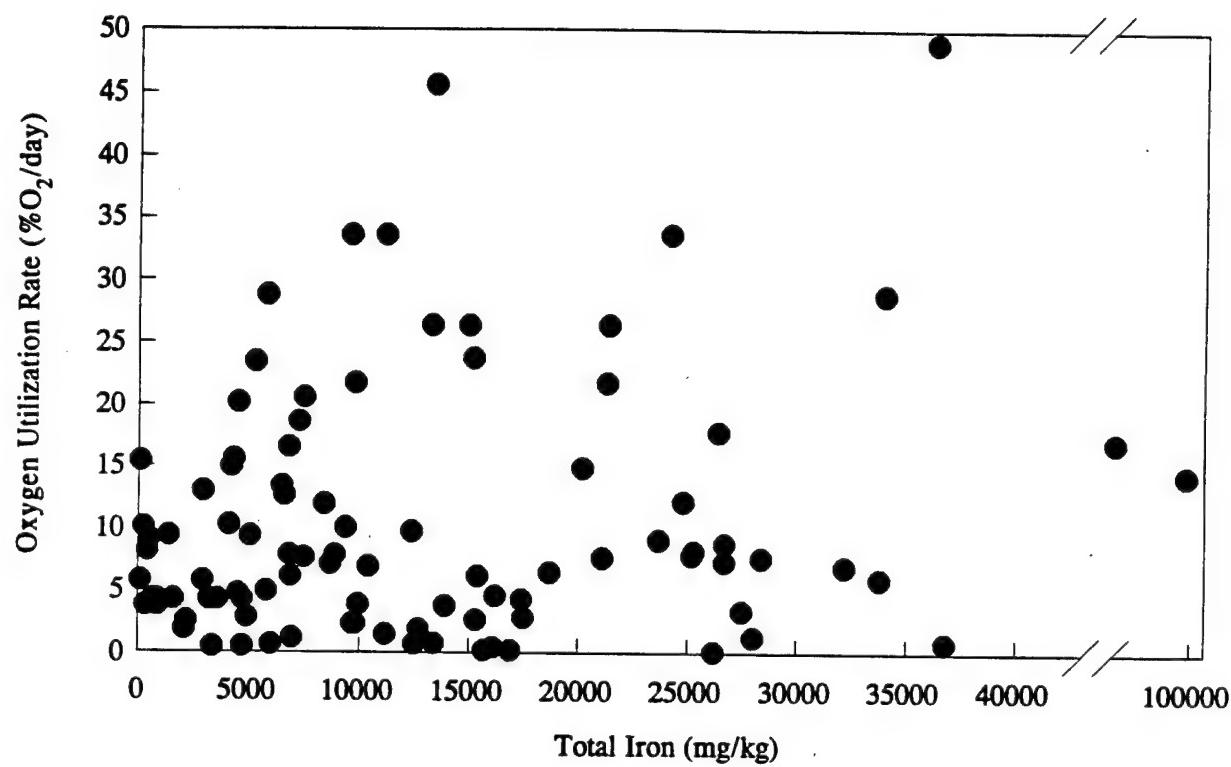


Figure 3-15. Correlation Between Oxygen Utilization Rates and Iron Content at Bioventing Initiative Sites

is occurring, and at lower concentrations less soil may be in direct contact with NAPLs. It is likely that the reduction in biodegradation rates observed over time on many sites is due at least in part to changes in the hydrocarbon makeup as the more degradable and more mobile compounds (i.e., benzene, toluene, ethylbenzene, and xylenes) are removed. At lower hydrocarbon concentrations where NAPLs are not present, a decline in rate would be expected with time as the available substrate is removed.

3.2.2.7 Bioavailability and Relative Biodegradability

Another critical parameter affecting the extent of in situ bioremediation is bioavailability of the contaminant(s) of concern. Bioavailability is a general term to describe the accessibility of contaminants to the degrading populations. Bioavailability consists of (1) a physical aspect related to phase distribution and mass transfer, and (2) a physiological aspect related to the suitability of the contaminant as a substrate (U.S. EPA, 1993, EPA/540/S-93/501). Compounds with greater aqueous solubilities and lower affinities to partition into NAPL or to sorb onto the soil generally are bioavailable to soil microorganisms and are more readily degraded. For example, BTEX is preferentially degraded relative to the larger alkanes found in fuels. The most likely explanation for this is that BTEX is more mobile and more soluble in pore water and therefore is more bioavailable.

3.3 Compounds Targeted for Removal

Any aerobically biodegradable compound, such as petroleum hydrocarbons, potentially can be degraded through bioventing. To date, bioventing has been applied primarily to petroleum hydrocarbons (Table 2-2); however, bioventing of PAHs (Lund et al., 1991; Hinchee and Ong, 1992; Alleman et al., 1995) and bioventing applied to an acetone, toluene, and naphthalene mixture (Leeson et al., 1994) have been implemented successfully.

The key to bioventing feasibility in most applications is biodegradability versus volatility of the compound. If the rate of volatilization greatly exceeds the rate of biodegradation, bioventing is unlikely to be successful, as removal occurs primarily through volatilization. This will occur most often in those cases where the contaminant is a fresh, highly volatile fuel. An unsuccessful bioventing application is unlikely to occur due to a lack of microbial activity. If bioventing is

operated in the injection mode as recommended by this manual, volatilized contaminants may be biodegraded before reaching the surface, unlike during an extraction operation¹. Figure 3-16 illustrates the relationship between a compound's physicochemical properties and its potential for bioventing.

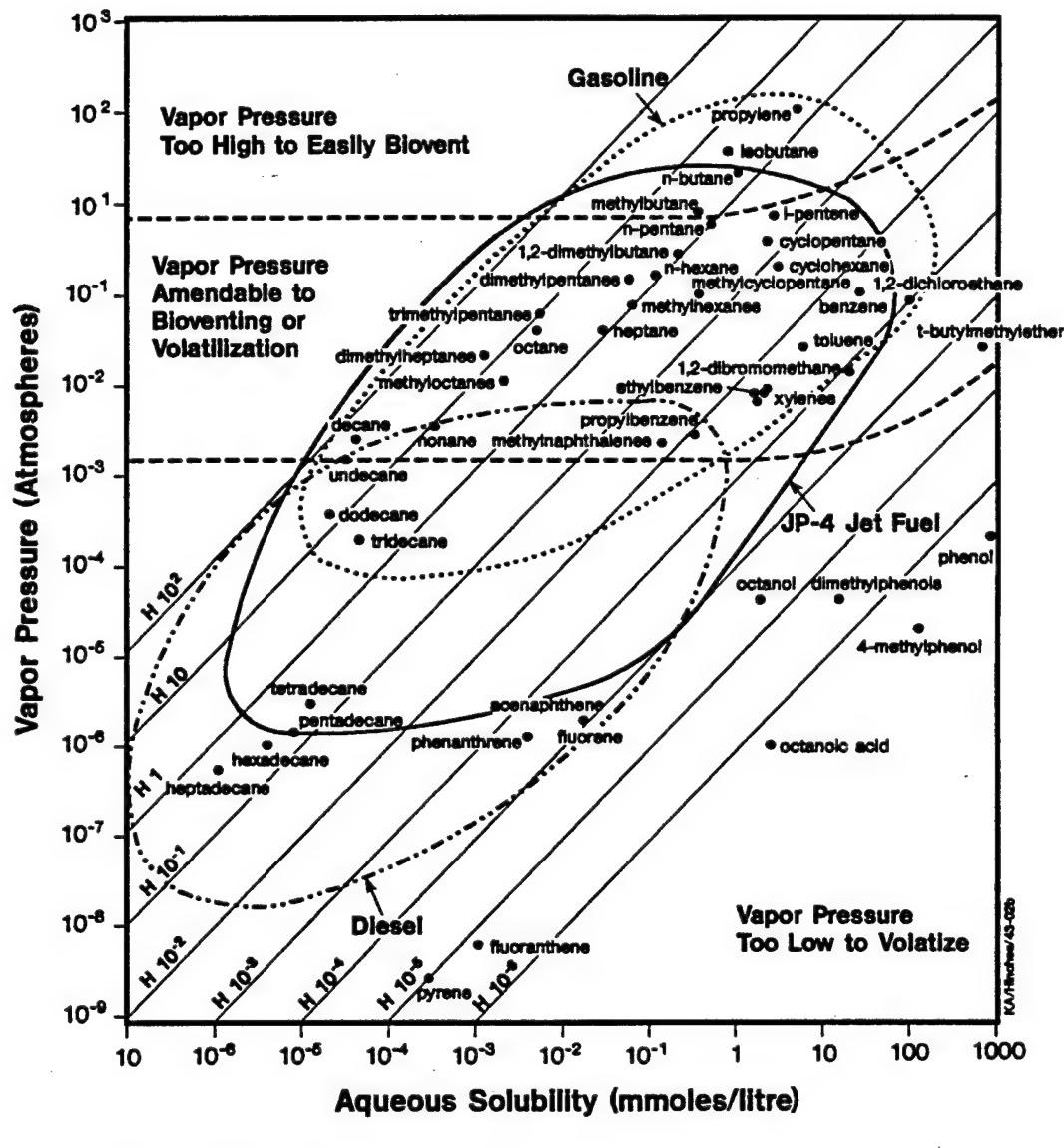
In general, compounds with a low vapor pressure² cannot be successfully removed by volatilization, but can be biodegraded in a bioventing application if they are aerobically biodegradable. High vapor pressure compounds are gases at ambient temperatures. These compounds volatilize too rapidly to be easily biodegraded in a bioventing system, but typically are a small component of fuels and, due to their high volatility, will attenuate rapidly. Compounds with vapor pressures between 1 and 760 mm Hg may be amenable to either volatilization or biodegradation. Within this intermediate range lie many of the petroleum hydrocarbon compounds of greatest regulatory interest, such as benzene, toluene, ethylbenzene, and the xylenes. As can be seen in Figure 3-16, various petroleum fuels are more or less amenable to bioventing. Some components of gasoline are too volatile to easily biodegrade, but, as stated previously, typically are present in low overall concentrations and are attenuated rapidly. Most of the diesel constituents are sufficiently nonvolatile to preclude volatilization, whereas the constituents of JP-4 jet fuel are intermediate in volatility.

To be amenable to bioventing, a compound must (1) biodegrade aerobically at a rate resulting in an oxygen demand greater than the rate of oxygen diffusion from the atmosphere, and (2) biodegrade at a sufficiently high rate to allow in situ biodegradation before volatilization. Practically, this means that low vapor pressure compounds need not biodegrade as rapidly as high vapor pressure compounds for bioventing to be successful. Figure 3-17 illustrates this relationship. The actual feasibility of bioventing is very site-specific and Figures 3-16 and 3-17 should not be used as absolutes, but rather as general guidelines.

Bioventing generally is not considered appropriate for treating compounds such as polychlorinated biphenyls (PCBs) and chlorinated hydrocarbons. However, through a cometabolic process, it may be possible to enhance the degradation of compounds such as TCE through

¹ Refer to Section 2.1, Volume II for a discussion of air injection versus extraction.

² For the purposes of this discussion, compounds with vapor pressures below approximately 1 mm Hg are considered low, and compounds with vapor pressures above approximately 760 mm Hg are considered high.



H = Henry's Law Coefficient (atm · m³/mole)

Figure 3-16. Relationship Between Contaminant Physicochemical Properties and Potential for Bioventing

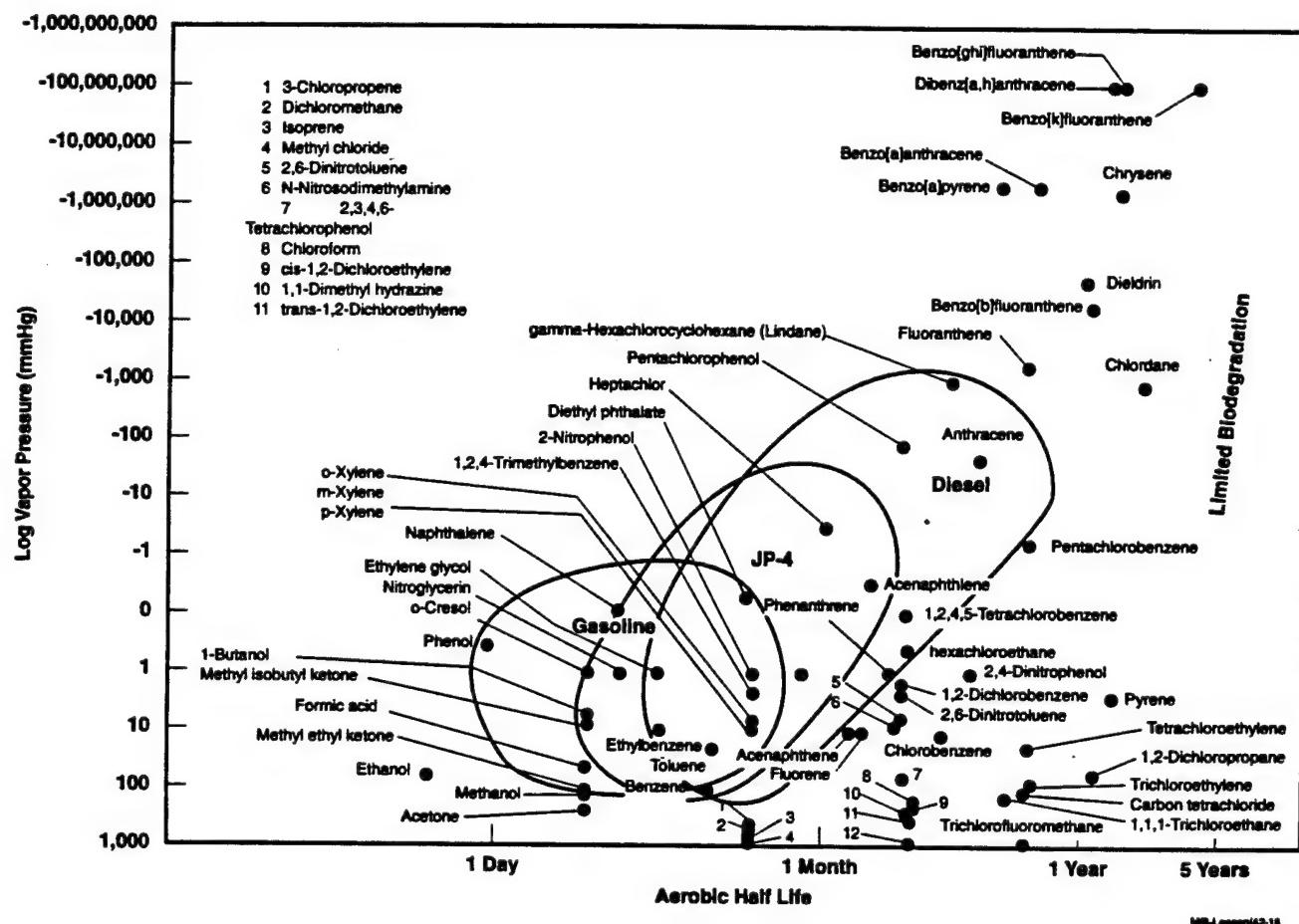


Figure 3-17. Relationship Between Contaminant Vapor Pressure and Aerobic Biodegradability

bioventing. In laboratory studies, it has been shown that if toluene is present to provide the primary source of carbon, organisms that grow on toluene may be able to cometabolize TCE (Wackett and Gibson, 1992). More recently, Hopkins et al. (1993) demonstrated TCE degradation in situ through the injection of oxygen and phenol into an aquifer. TCE removal of 88% was observed in the field indicating the potential for cometabolic degradation of chlorinated compounds in situ.

3.4 BTEX Versus TPH Removal in Petroleum-Contaminated Sites

BTEX generally are the compounds that are regulated most stringently. Typically, these compounds degrade very rapidly during bioventing, and at most sites, are degraded to below detection limits within 1 year of operation of a bioventing system. This trend was illustrated in a study at Tyndall AFB¹ and has been confirmed at 81 sites completing the 1-year testing under the Bioventing Initiative. At Tyndall AFB, two test plots were studied with initial hydrocarbon concentrations of 5,100 and 7,700 mg/kg. After 9 months of bioventing, TPH was reduced by 40% from the initial concentration. However, the low-molecular-weight compounds such as BTEX were reduced by more than 90% (Figure 3-18). The low-molecular-weight compounds were preferentially degraded over the heavier fuel components, which is consistent with previous research (Atlas, 1986).

If a risk-based approach to remediation is used that focuses on removing the soluble, mobile, and more toxic BTEX components of the fuel, remediation times can be reduced significantly, making bioventing an attractive technology for risk-based remediations. In addition, the BTEX compounds often are initially at relatively low levels at many fuel-contaminated sites as illustrated by results from the Bioventing Initiative. Data collected from the majority of the Bioventing Initiative sites demonstrate that more than 85% of initial soil samples contained less than 1 mg/kg of benzene (Figure 3-19). An exception to this may be gasoline-contaminated sites; the majority of sites included in the Bioventing Initiative were contaminated with heavier weight contaminants. Only 19 of 125 Bioventing Initiative sites were contaminated by gasoline or AVGAS.

¹ Refer to Section 4.2 for a case history of the bioventing study at Tyndall AFB, Florida.

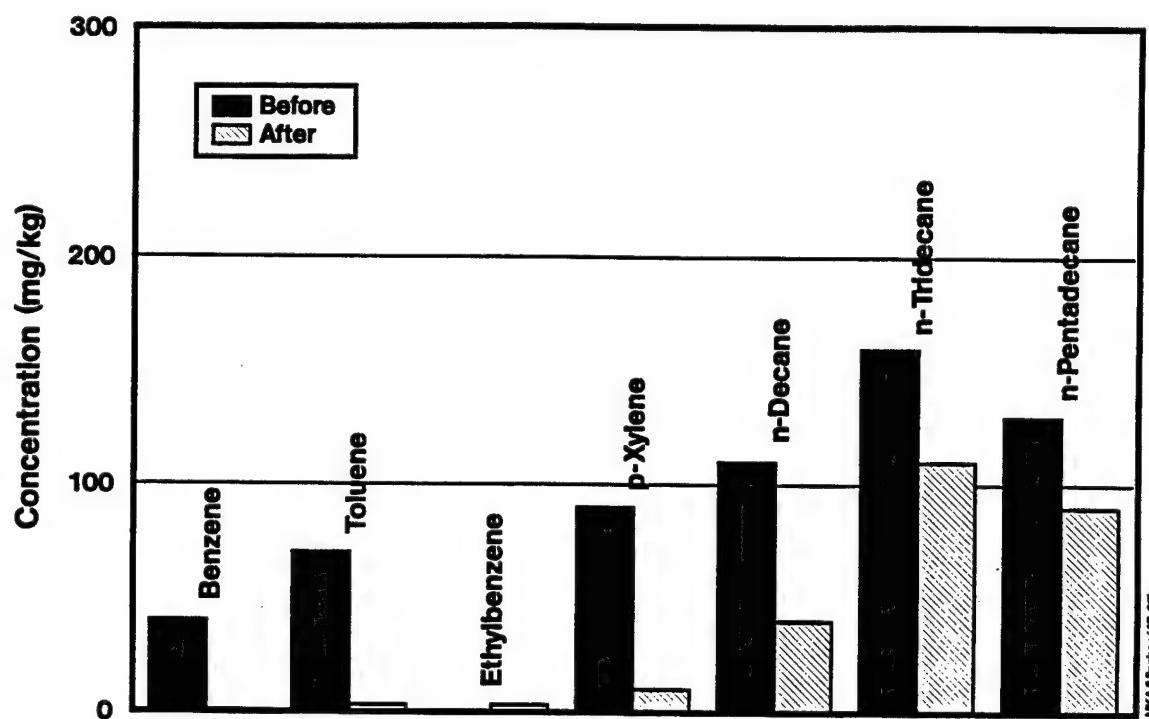


Figure 3-18. Results of Soil Analysis Before and After Venting from Plot V2 at Tyndall AFB, Florida

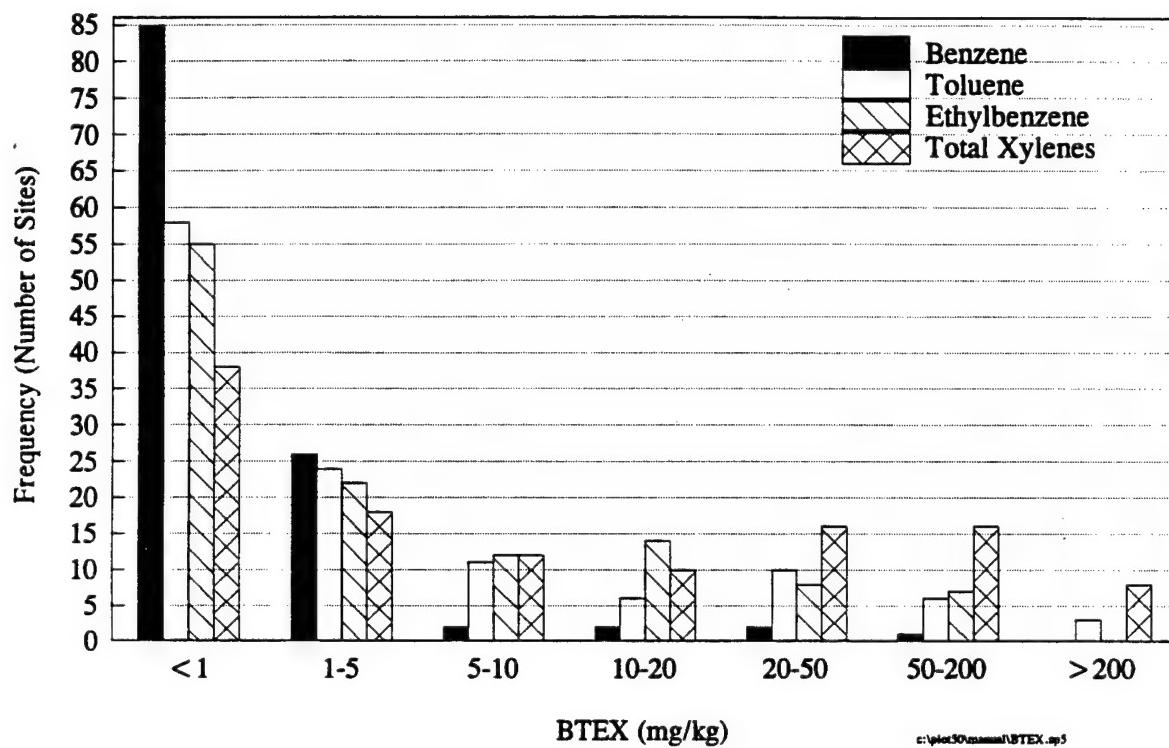


Figure 3-19. Contaminant Distribution at Bioventing Initiative Sites

4.0 BIOVENTING CASE HISTORIES

Four of the first well-documented bioventing studies are presented in this section to illustrate significant results which have contributed to the development of bioventing, the Bioventing Initiative, and this document. The development of the Bioventing Initiative was based largely upon the results from these four early studies, which are discussed in detail in this section. Site 914, Hill AFB, Utah, was one of the first bioventing systems studied. This study was designed to examine the feasibility of biodegradation through air injection, and also to investigate the effect of nutrient and moisture addition on biodegradation. The second site was a bioventing system at Tyndall AFB, Florida, initiated in 1990. This study was short-term (9 months), but was designed to examine process variables in more detail than was possible at Site 914, Hill AFB. The third site discussed in this chapter was conducted at Site 280, Hill AFB, Utah. This study was initiated in 1991 as a bioventing site and was operated for approximately 3 years. Research on air flowrates and injection depth was carried out at this site. The fourth study presented in this chapter was conducted at Eielson AFB, Alaska. This study was initiated in 1991 as a bioventing system and was operated for 3 years. This study was conducted to examine the feasibility of bioventing in a subarctic climate as well as to evaluate the effects of soil warming on biodegradation rates.

A case history of the Fire Training Area, Battle Creek Air National Guard Base (ANGB) also is presented in this chapter. This site was included in the Bioventing Initiative, but additional samples were collected at the end of the 1-year study as part of a separate project. The results from this study illustrate typical installations and results from a Bioventing Initiative site, and provide additional data on BTEX contamination after 1 year of bioventing.

These case histories are not presented as design examples, because they were designed as research efforts. In fact, these studies have been the basis for development of current design practice as presented in Volume II of this document. Details of each of these studies are presented in the following sections.

4.1 Site 914, Hill AFB, Utah

A spill of approximately 27,000 gallons of JP-4 jet fuel occurred at Site 914 when an automatic overflow device failed. Contamination was limited to the upper 65 ft (20 m) of a delta outwash of the Weber River. This surficial formation extends from the surface to a depth of approximately 65 ft (20 m) and is composed of mixed sand and gravel with occasional clay stringers.

Depth to regional groundwater is approximately 600 ft (180 m); however, water occasionally may be found in discontinuous perched zones. Soil moisture averaged less than 6% by weight in the contaminated soils.

The collected soil samples had JP-4 jet fuel concentrations up to 20,000 mg/kg, with an average concentration of approximately 400 mg/kg (Oak Ridge National Laboratory, 1989). Contaminants were unevenly distributed to depths of 65 ft (20 m). Vent wells were drilled to approximately 65 ft (20 m) below the ground surface and were screened from 10 to 60 ft (3 to 20 m) below the surface. A background vent well was installed in an uncontaminated location in the same geologic formation approximately 700 ft (210 m) north of the site.

This system originally was designed for SVE, not for bioventing. During the initial 9 months of operation, it was operated to optimize volatilization, while biodegradation was merely observed. After this period, air flowrates were greatly reduced, and an effort was made to optimize biodegradation and limit volatilization.

Soil vapor extraction was initiated in December 1988 at a rate of approximately 25 cubic ft per minute (cfm) (710 L/min). The off-gas was treated by catalytic incineration, and initially it was necessary to dilute the highly concentrated gas to remain below explosive limits and within the incinerator's hydrocarbon operating limits. The venting rate was gradually increased to approximately 1,500 cfm (4.2×10^4 L/min) as hydrocarbon concentrations dropped. During the period between December 1988 and November 1989, more than 3.5×10^8 ft³ (9.9×10^{10} L) of soil gas were extracted from the site.

In November 1989, ventilation rates were reduced to between approximately 300 and 600 cfm (8,500 to 17,000 L/min) to provide aeration for bioremediation while reducing off-gas generation. This change allowed removal of the catalytic incinerators, saving approximately \$13,000 per month in rental and propane costs.

Hinchee and Arthur (1991) conducted bench-scale studies using soils from this site and found that, in the laboratory, both moisture and nutrients appeared to become limiting after aerobic conditions had been achieved. These findings led to the addition of first moisture and then nutrients in the field. Moisture addition clearly stimulated biodegradation, whereas nutrient addition did not (Figure 4-1). The failure to observe an effect of nutrient addition could be explained by a number of factors:

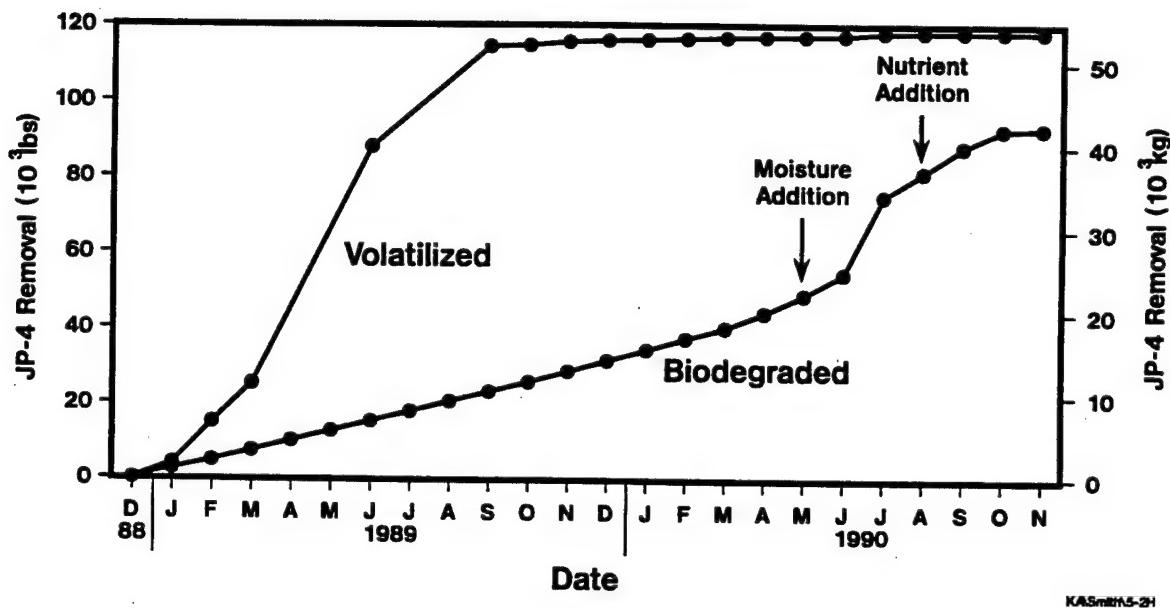


Figure 4-1. Cumulative Hydrocarbon Removal and the Effect of Moisture and Nutrient Addition at Site 914, Hill AFB, Utah

1. The nutrients failed to move in the soils, which is a problem particularly for ammonia and phosphorus (Aggarwal et al., 1991).
2. Remediation of the site was entering its final phase and nutrient addition may have been too late to result in an observed change.
3. Nutrients simply may have not been limiting.

During extraction, oxygen and hydrocarbon concentrations in the off-gas were measured. To quantify the extent of biodegradation at the site, the oxygen was converted to an equivalent basis. This was based on the stoichiometric oxygen requirement for hexane mineralization¹. Hydrocarbon concentrations were determined based on direct readings of a total hydrocarbon analyzer calibrated to hexane. Based on these calculations, the mass of JP-4 jet fuel as carbon removed was approximately 1,500 pounds volatilized and 93,000 pounds biodegraded (Figure 4-1). After a 2-year period, cleanup and regulatory closure were achieved (Figure 4-2).

The results of this study indicated that aerobic biodegradation of JP-4 jet fuel did occur in the vadose zone at Site 914. Biodegradation was increased by soil venting at this site because, prior to venting, biodegradation appeared to have been oxygen limited. The SVE system, designed to volatilize the fuel, stimulated in situ biodegradation with no added nutrients or moisture. In this study, approximately 15% of the documented field removal observed at the site was the result of microbial-mediated mineralization to carbon dioxide. Additional biological fuel removal by conversion to biomass and degradation products no doubt occurred, but was not quantified.

From this study, it was apparent that further studies of field biodegradation in unsaturated soils were needed to develop a better understanding of the effects of such variables as oxygen content, nutrient requirements, soil moisture, contaminant levels, and soil type on the limitation and optimization of bioventing of contaminated field sites. Also, further studies of gas transport in the vadose zone were needed to ensure adequate design of air delivery systems.

Further details of this study may be found in Dupont et al. (1991) and Hinchee et al. (1991b).

¹ Refer to Section 3.3, Volume II for a discussion of this calculation.

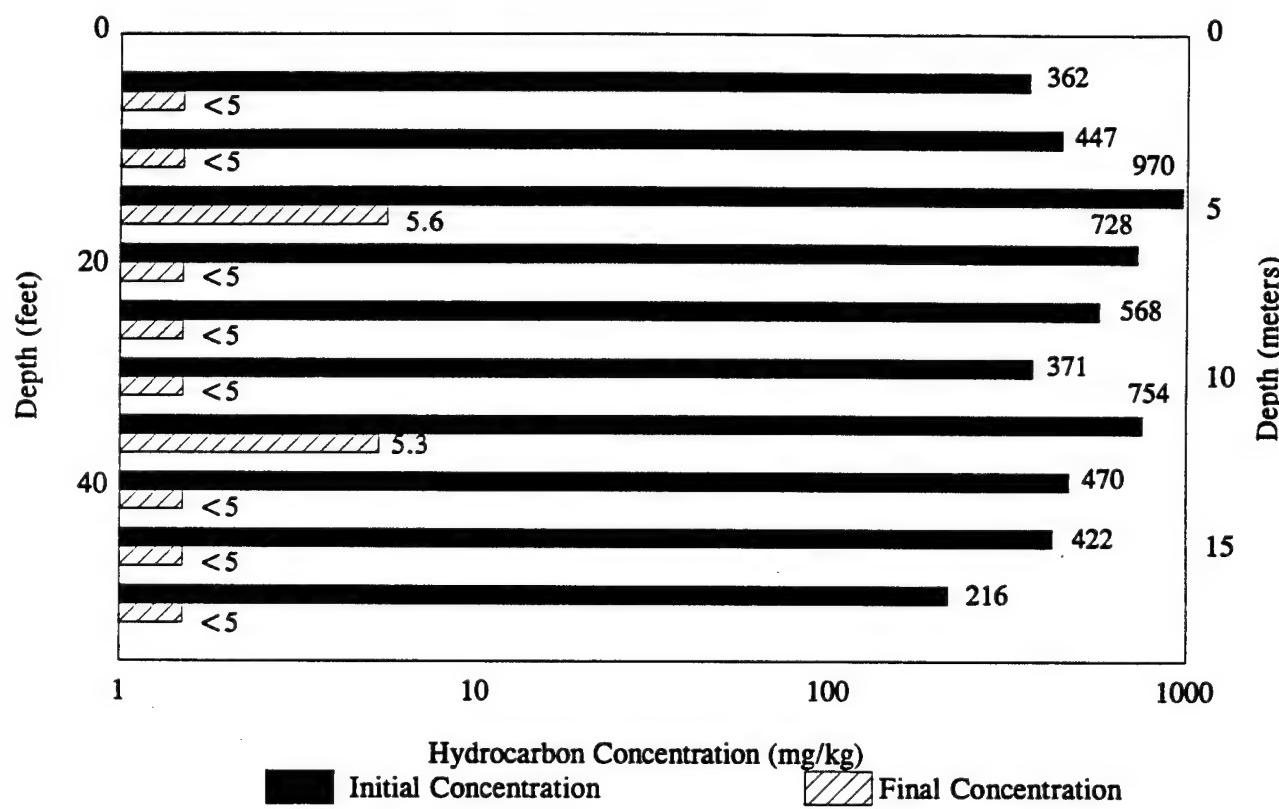


Figure 4-2. Results of Soil Analysis Before and After Treatment at Site 914, Hill AFB, Utah

4.2 Tyndall AFB, Florida

A more controlled study than was possible at Site 914, Hill AFB was designed at Tyndall AFB as a follow-up to the Hill AFB research. The experimental area in the Tyndall AFB study was located at a site where past JP-4 jet fuel storage had resulted in contaminated soils. The nature and volume of fuel spilled or leaked were unknown. The site soils were a fine- to medium-grained quartz sand. The depth to groundwater was 2 to 4 ft (0.61 to 1.2 m).

The field study was designed with the following objectives:

- to determine whether bioventing enhanced biodegradation of JP-4 jet fuel at this site;
- to determine whether moisture addition coupled with bioventing enhanced biodegradation rates;
- to determine whether nutrient addition coupled with bioventing enhanced biodegradation rates;
- to evaluate flowrate manipulation to maximize biodegradation and minimize volatilization; and
- to calculate specific biodegradation rate constants from a series of respiration tests conducted during shutdown of the air extraction system.

Four test cells were constructed to allow control of gas flow, water flow, and nutrient addition. Test cells V1 and V2 were installed in the hydrocarbon-contaminated zone; test cells V3 and V4 were installed in uncontaminated soils. Test cells were constructed and operated in the following manner:

- V1 (uncontaminated): Venting for approximately 8 weeks, followed by moisture addition for approximately 14 weeks, followed by moisture and nutrient addition for approximately 7 weeks.
- V2 (uncontaminated): Venting coupled with moisture and nutrient addition for 29 weeks.
- V3 (uncontaminated): Venting with moisture and nutrient addition at rates similar to V2, with injection of hydrocarbon-contaminated off-gas from V1. Operation was conducted at a series of flowrates and retention times.

- V4 (uncontaminated): Venting with moisture and nutrient addition at rates similar to V2.

Initial site characterization indicated the mean soil hydrocarbon levels were 5,100 and 7,700 mg of hexane-equivalent/kg in treatment plots V1 and V2, respectively. The contaminated area was dewatered, and hydraulic control was maintained to keep the depth to water at approximately 5.25 ft (1.6 m). This exposed more of the contaminated soil to aeration. During normal operation, air flowrates were maintained at approximately one air-filled void volume per day.

Biodegradation and volatilization rates were much higher at the Tyndall AFB site than those observed at Hill AFB. These higher rates were likely due to higher average levels of contamination, higher temperatures, and higher moisture content. Biodegradation rates during bioventing ranged from approximately 2 to 20 mg/kg-day, with average values of 5 mg/kg-day. After 200 days of aeration, an average hydrocarbon reduction of approximately 2,900 mg/kg was observed. This represented a reduction in total hydrocarbons of approximately 40%.

Another important observation of this study was the effect of temperature on the biodegradation rate. Miller (1990) found that the van't Hoff-Arrhenius equation provided an excellent model of temperature effects. In the Tyndall AFB study, soil temperature varied by only approximately 7°C (44.6°F), yet biodegradation rates were approximately twice as high at 25°C (77°F) than at 18°C (64.4°F).

Operational data and biodegradation rates indicated that soil moisture and nutrients were not limiting factors in hydrocarbon biodegradation for this site (Figure 4-3). The lack of moisture effect contrasts with the Hill AFB findings, but most likely is the result of contrasting climatic and hydrogeologic conditions. Hill AFB is located in a high-elevation desert with a very deep water table. Tyndall AFB is located in a moist, subtropical environment, and at the site studies, the water table was maintained at a depth of approximately 5.25 ft (1.6 m). The nutrient findings support field observations at Hill AFB that the addition of nutrients does not stimulate biodegradation. Based on acetylene reduction studies, Miller (1990) speculated that adequate nitrogen was present due to nitrogen fixation. Both the Hill and Tyndall AFB sites had been contaminated for several years before the bioventing studies began, and both sites were anaerobic. It is possible that nitrogen fixation, which is maximized under these conditions, provided the required nutrients.. In any case, these findings show that nutrient addition is not always required.

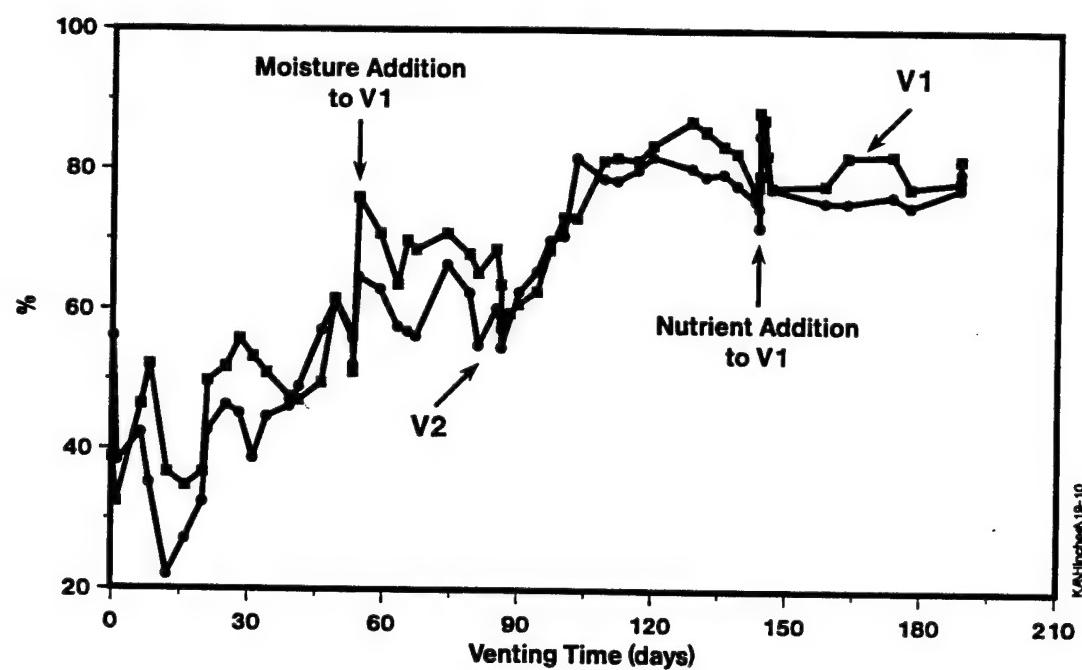


Figure 4-3. Cumulative Percent Hydrocarbon Removal and the Effect of Moisture and Nutrient Addition at Tyndall AFB, Florida

In the Tyndall AFB study, a careful evaluation of the relationship between air flowrates and biodegradation and volatilization was made. It was found that extracting air at the optimal rate for biodegradation resulted in 90% removal by biodegradation and 10% removal by volatilization. It was also found that passing the contaminants volatilized in the off-gas through clean soil resulted in complete biodegradation of the volatilized vapors.

In situ respiration tests documented that oxygen consumption rates followed zero-order kinetics and that rates were linear down to 2 to 4% oxygen. Therefore, air flowrates can be minimized to maintain oxygen levels between 2 and 4% without inhibiting biodegradation of fuel, with the added benefit that lower air flowrates will increase the percent of removal by biodegradation and decrease the percent of removal by volatilization.

The study was terminated because the process monitoring objectives had been met; biodegradation was still vigorous. Although the TPH had been reduced by only 40% by the time of study termination, the low-molecular-weight aromatics — the BTEX components — were reduced by more than 90% (Figure 3-18). It appeared that the bioventing process more rapidly removed the BTEX compounds than the other JP-4 fuel constituents.

Results from this study demonstrated the effectiveness of bioventing for remediating fuel-contaminated soils, the ineffectiveness of moisture or nutrient addition for increasing in situ biodegradation rates, and the importance of air flowrates for optimizing biodegradation over volatilization. However, it was evident from this study that a long-term bioventing study was necessary to examine process variables. This led to the initiation of the Site 280, Hill AFB and the Site 20, Eielson AFB projects described in the following sections.

Further details of the Tyndall AFB study may be found in Miller (1990) and Miller et al. (1991).

4.3 Site 280, Hill AFB, Utah

A key objective of the study at Site 280 was to optimize the injection air flowrates. These efforts were intended to maximize biodegradation rates in JP-4 jet fuel-contaminated soils while minimizing or eliminating volatilization. The site studied was a JP-4 jet fuel spill at Hill AFB that had existed since sometime in the 1940s (Figure 4-4). The geology was similar to that of Site 914, but the average contaminant levels were slightly higher (Figure 4-5). Vent wells were installed to a

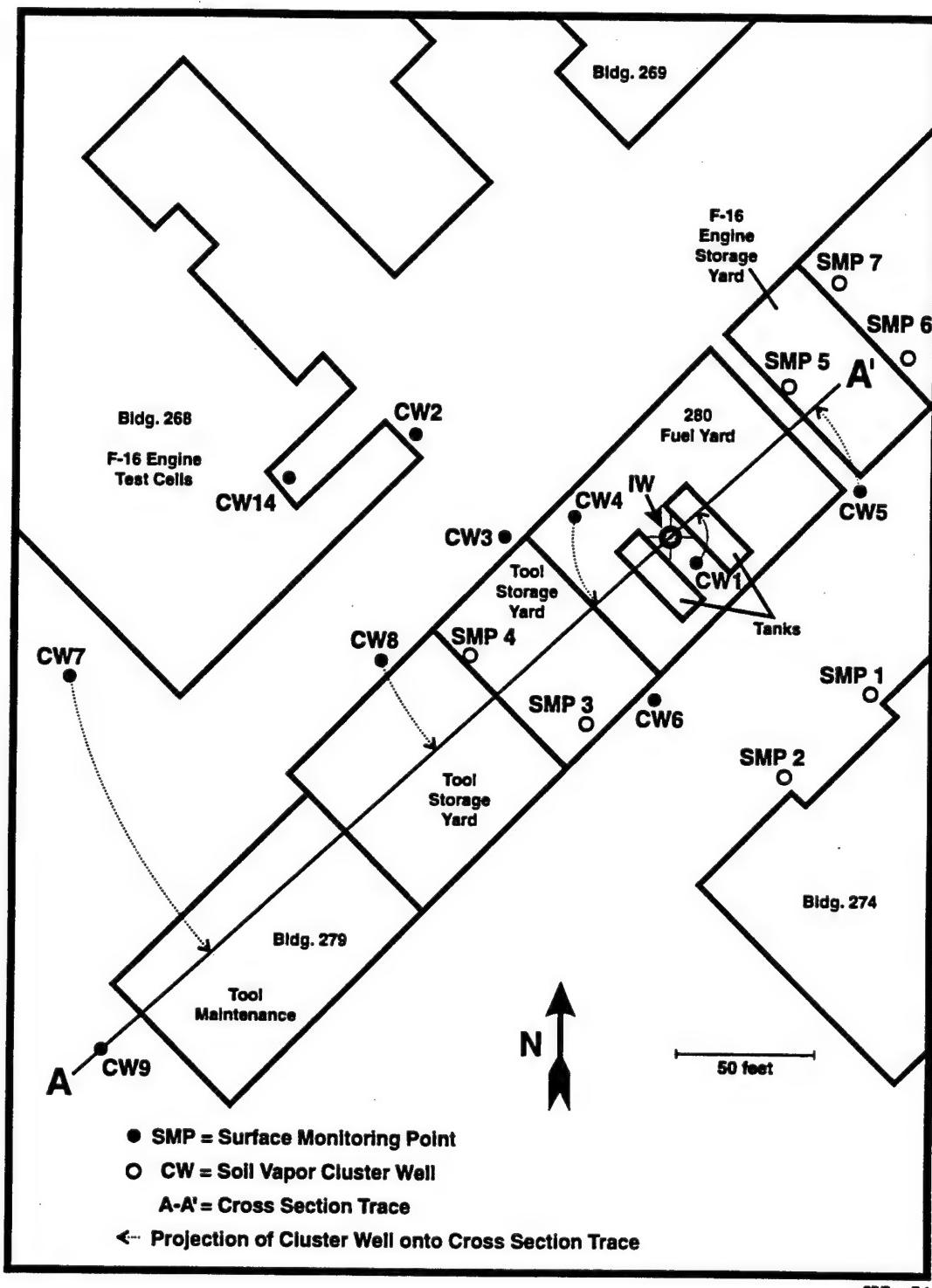


Figure 4-4. Schematic Diagram Showing Locations of Soil Gas Monitoring Points, Surface Monitoring Points, and Injection Wells at Site 280, Hill AFB, Utah

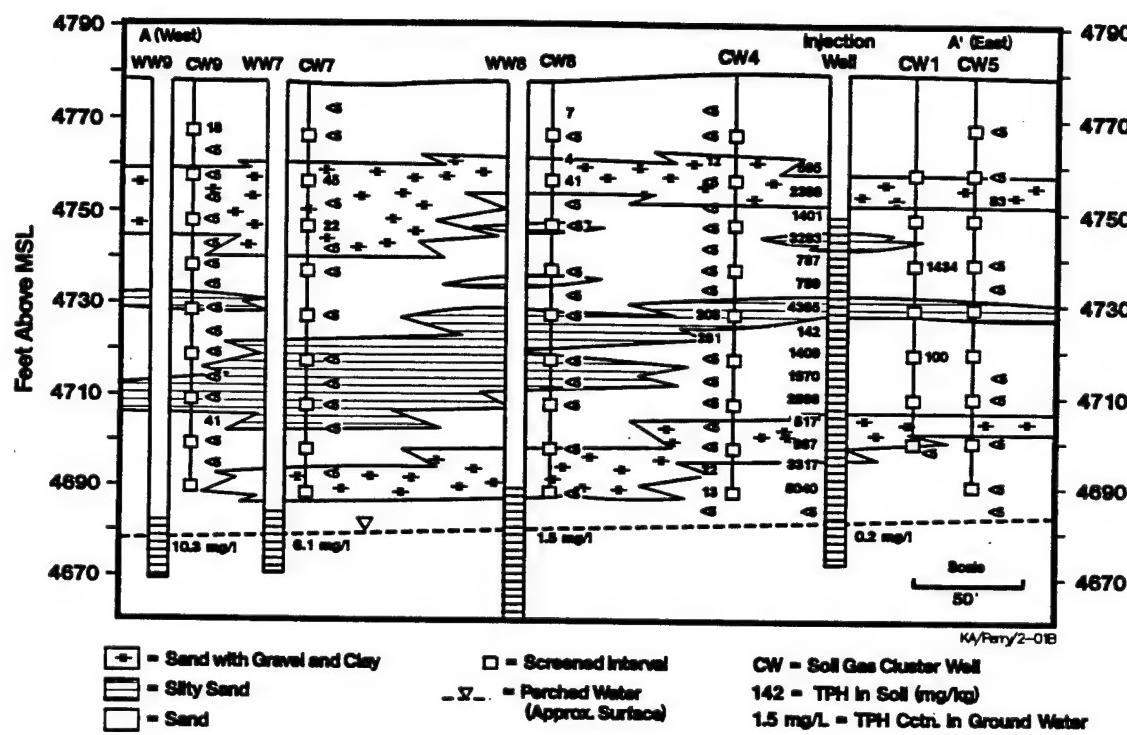


Figure 4-5. Geologic Cross Section Showing Known Geologic Features and Soil TPH Concentrations (mg/kg) at Site 280, Hill AFB, Utah

depth of approximately 110 ft and groundwater was at a depth of approximately 100 ft.

From November 1992 through January 1995, a number of studies were conducted to evaluate low-intensity bioremediation at Site 280. These efforts included (1) varying the air injection flowrates in conjunction with in situ respiration tests, and (2) surface emissions testing to provide information for system optimization.

Five air flowrate evaluations were conducted at Site 280 from 1991 through 1994 (28, 67, 67, 40, and 117 cfm [790, 1,900, 1,900, 1,100, and 3,300 L/min]). Each evaluation was followed by in situ respiration testing. The 67 cfm (1,900 L/min) study was repeated to include additional soil gas monitoring points added to the site. Monthly soil gas monitoring was conducted at Site 280 to measure the concentrations of oxygen, carbon dioxide, and TPH at each sampling point following system operation at each of the different air flowrates.

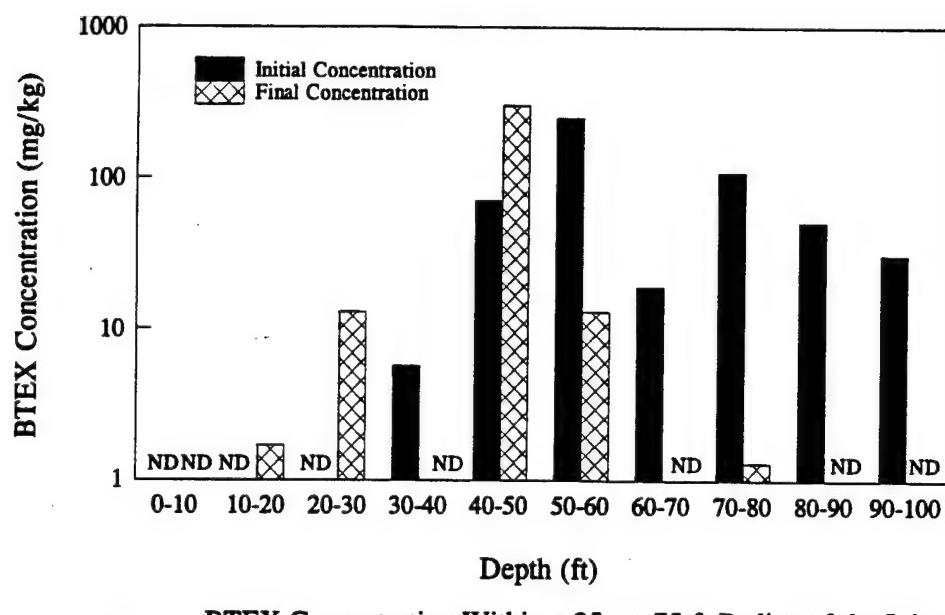
Surface emissions tests were conducted during each air injection test and while the air injection system was turned off. In each of the surface emissions tests, no significant differences were found between the periods of air injection and no air injection. TPH soil gas levels measured during the air injection periods averaged approximately 70 ppmv, while TPH soil gas levels during resting periods averaged 42 ppmv. These averages were not found to be statistically different. Likewise, surface emissions rates were not significantly different at different flowrates.

Final soil sampling was conducted in December 1994. Results from the initial and final BTEX and TPH samples are shown in Figures 4-6 and 4-7, respectively. Results shown represent soil samples within a 0- to 25-ft radius of the injection well and a 25- to 75-ft radius. In general, BTEX and TPH concentrations decreased at all depths within the 25-ft radius from the vent well, with the exception of the samples collected at a depth of 90 to 100 ft. Samples taken from this depth are located at the capillary fringe, and it is likely that adequate aeration was not possible at that location. Samples collected beyond the 25-ft radius were less conclusive, indicating that this area was not aerated.

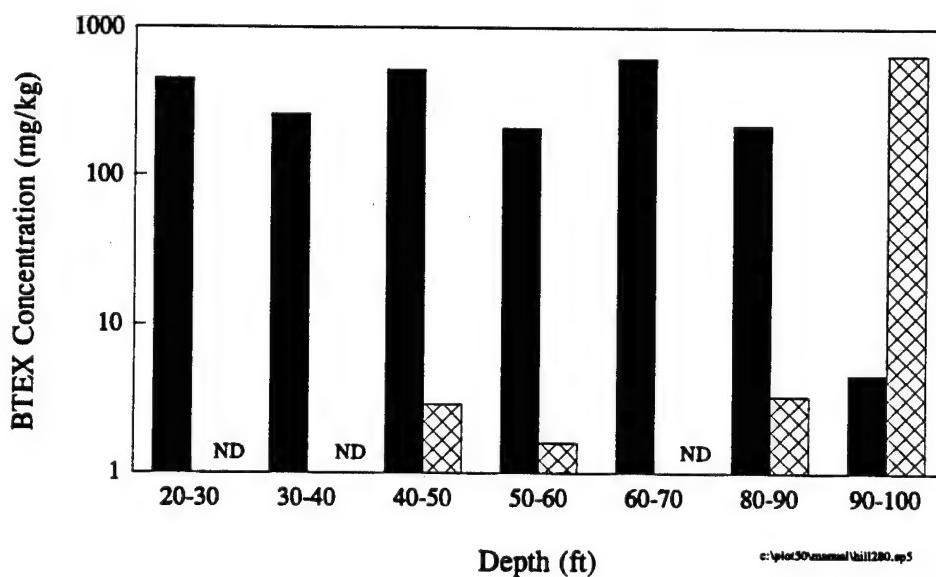
Further details of the Site 280, Hill AFB study may be found in Sayles et al. (1994b).

4.4 Site 20, Eielson AFB, Alaska

The objective of the Eielson AFB study was to install and operate an in situ soil bioremediation system to investigate the feasibility of using bioventing to remediate JP-4 jet fuel

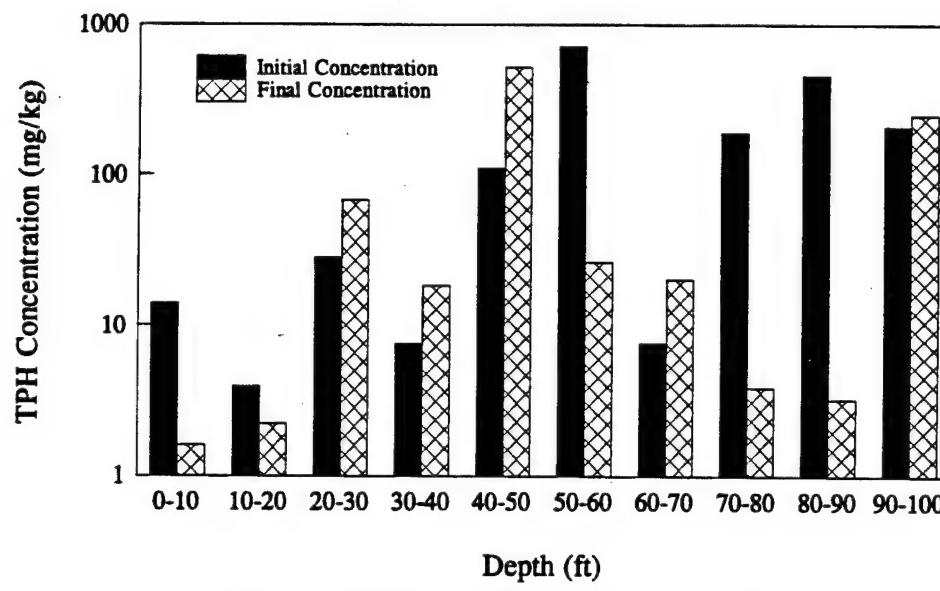


a. BTEX Concentration Within a 25- to 75-ft Radius of the Injection Well

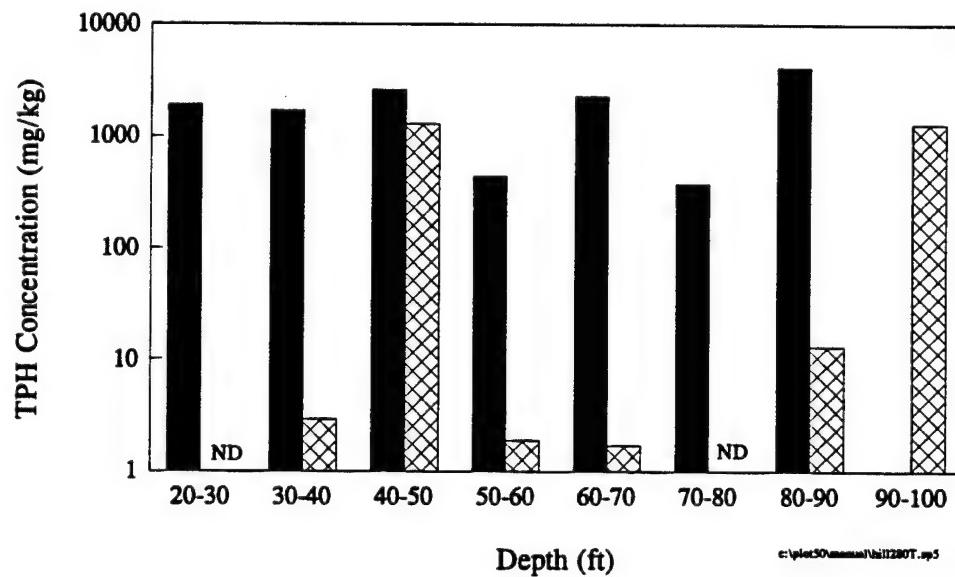


b. BTEX Concentration Within a 0- to 25-ft Radius of the Injection Well

Figure 4-6. Site Average Initial and Final BTEX Soil Sample Results at Site 280, Hill AFB, Utah



a. TPH Concentration Within a 25- to 75-ft Radius of the Injection Well



b. TPH Concentration Within a 0- to 25-ft Radius of the Injection Well

Figure 4-7. Site Average Initial and Final TPH Soil Sample Results at Site 280, Hill AFB, Utah

contamination in a subarctic environment and to actively increase soil temperature to determine to what degree increased soil temperature can enhance the biodegradation rates of JP-4 contaminants in soil. This study comprised four test plots: (1) one in which heated groundwater was circulated through the test plot (active warming test plot); (2) one in which plastic sheeting was placed over the ground surface of the test plot during the spring and summer months to capture solar heat and passively warm the soil (passive warming test plot); (3) one in which heat tape was installed in the test plot to heat the soil directly (surface warming test plot); and (4) a control test plot, which received air injection but no soil warming (control test plot). In addition, an uncontaminated background location also received air injection but no soil warming to monitor natural background respiration rates. The site soils were a sandy silt, with increasing amounts of sand and gravel with depth. Groundwater was typically at approximately the 7-ft depth. Figure 4-8 illustrates site geologic features and typical construction details of site installations.

Differences in soil temperatures were significant among the four test plots (Figure 4-9). When in operation, the active warming test plot consistently maintained higher temperatures than the other test plots during the winter months. In the passive warming test plot, plastic sheeting increased soil temperature, with average soil temperatures as high at 18°C (64.4°F) during the summer months, compared to average temperatures of approximately 10°C (50°F) in the control test plot. A significant feature of this soil warming technique was that the addition of plastic sheeting in the spring caused a rapid increase in soil temperature, nearly 6 to 8 weeks sooner than in the unheated test plots. The early heating significantly increased the period of rapid microbial degradation. During the winter months, the passive warming test plot remained warmer than the control test plot.

Respiration rates were measured quarterly in each test plot. Of particular interest were rates measured in the control test plot. It was expected that no substantial microbial activity would occur during the winter months in unheated test plots due to the extreme temperatures. However, significant microbial activity was consistently measured in the control test plot, even at soil temperatures just below freezing (Figure 4-10). Respiration rates in the passive warming test plot were observed to increase nearly one order of magnitude as soil temperature increased during the summer months, indicating the success of the use of plastic sheeting to promote soil warming (Figure 4-10). Respiration rates measured in the active warming test plot were higher than those measured in the passive warming or control test plot when warm water circulation was operating. Warm water circulation was discontinued in fall 1993, and as the soil temperature dropped, no significant

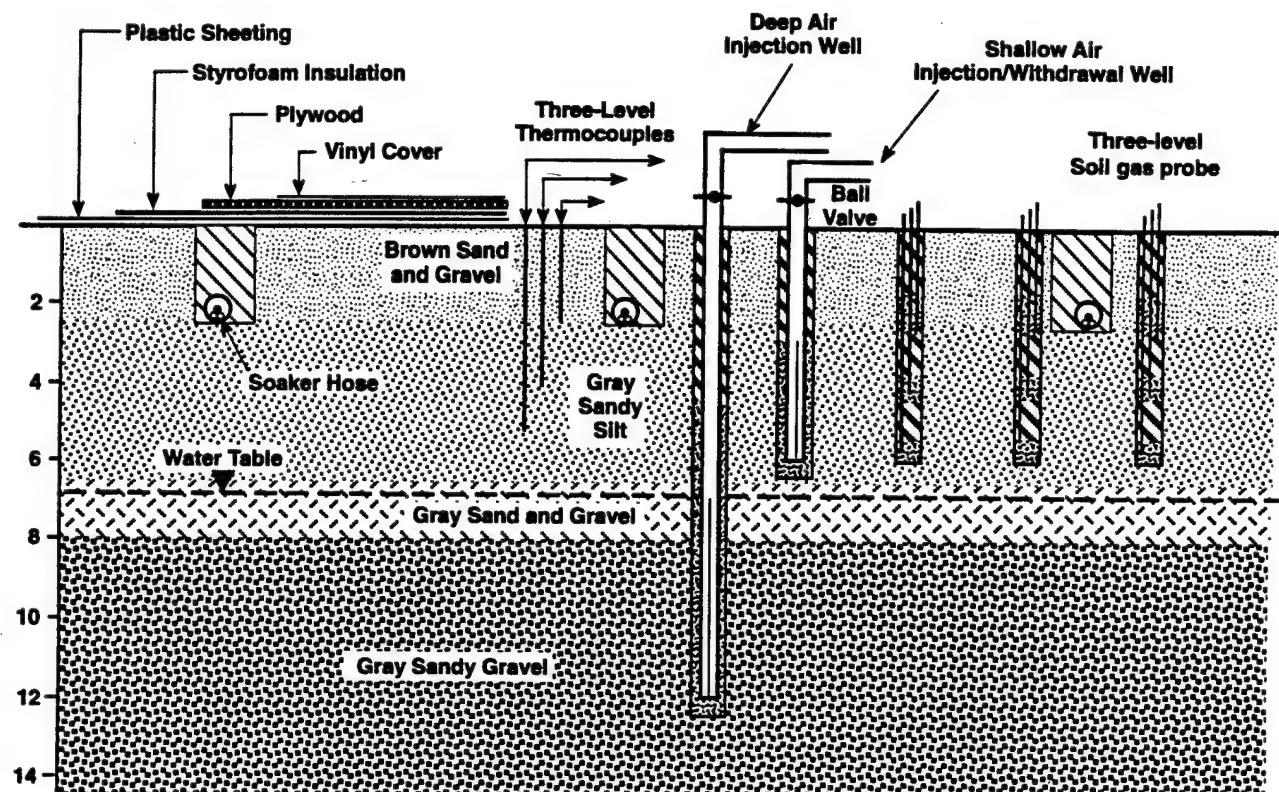


Figure 4-8. Cross Section Showing Geologic Features and Typical Construction Details of the Active Warming Test Plot, Site 20, Eielson AFB, Alaska

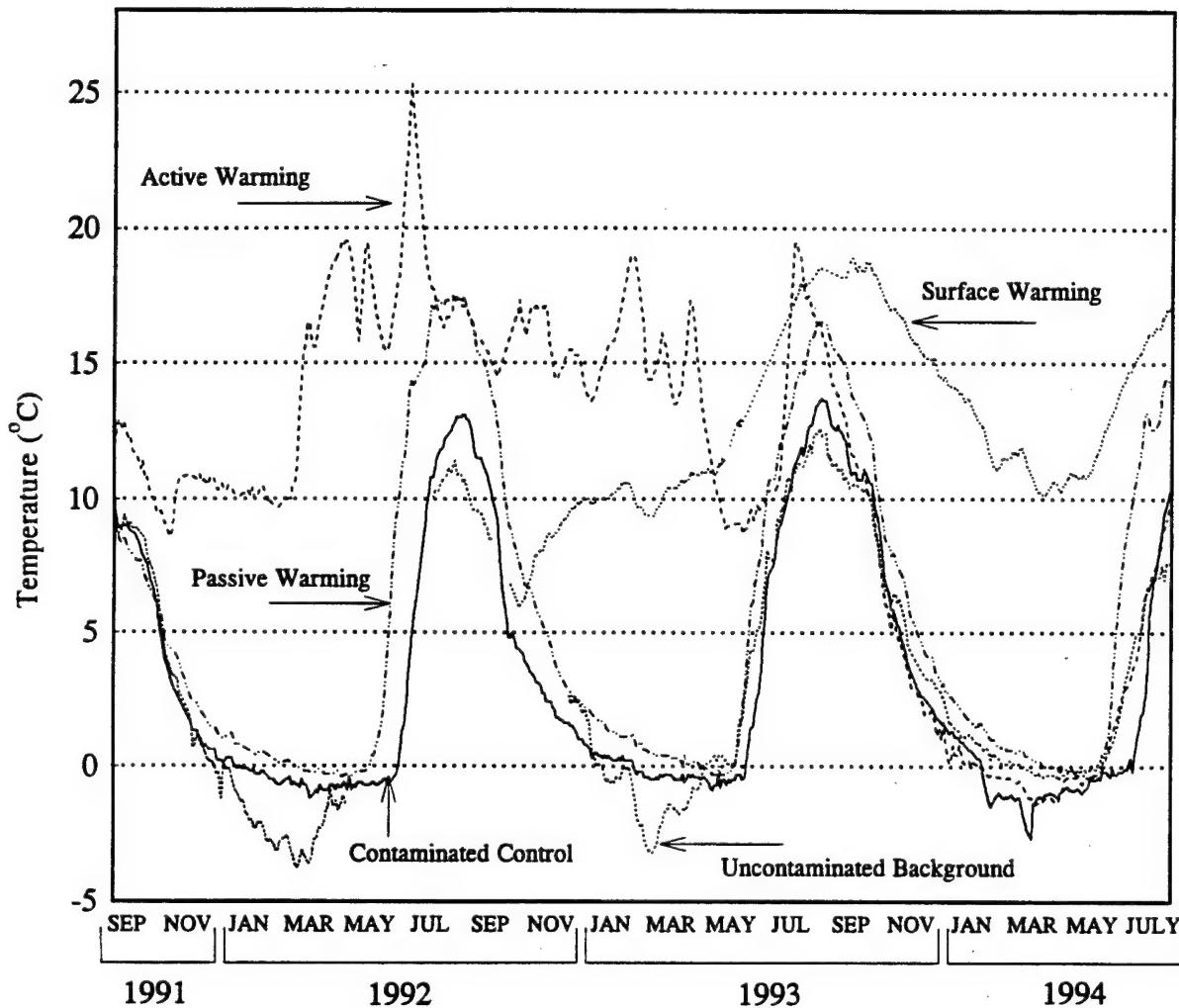


Figure 4-9. Soil Temperature in Four Test Plots and the Background Area at Site 20, Eielson AFB, Alaska

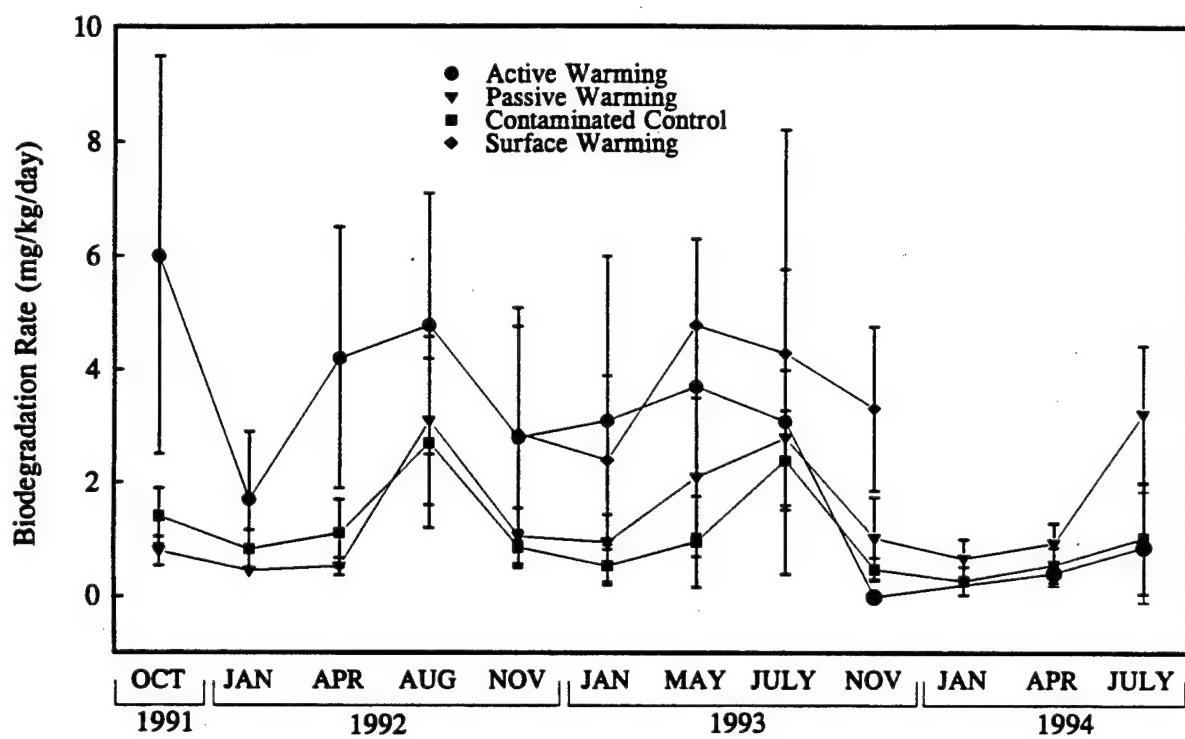


Figure 4-10. Biodegradation Rates in Four Test Plots at Site 20, Eielson AFB, Alaska

microbial activity could be measured in the test plot during the winter months. This phenomenon is interesting in that it suggests that during the 2 years of soil heating, microorganisms adapted to growth at higher temperatures, yet lost the ability to remain active in colder soils. In order to determine whether the microbial population could adapt to cold temperatures given time, a final *in situ* respiration test was conducted in January 1995. Significant microbial activity was measured, comparable to the control test plot, indicating either readaptation or recolonization by the microbial population.

The surface warming test plot has shown promise as a form of soil warming. Soil temperatures and respiration rates were higher than temperatures or rates in either the passive warming or control test plot and were similar to those measured in the active warming test plot during warm water circulation. These results indicate that the use of heat tape may prove to be a more efficient means of soil warming than hot water circulation, because the problem of high soil moisture content is avoided.

An evaluation of cost versus remediation time was conducted to evaluate the feasibility of soil warming. Costs for the basic bioventing system in Table 4-1 were based on costs calculated by Downey et al. (1994). Given that average biodegradation rates were higher in the actively warmed plots, overall remediation time would be more rapid than in the unheated test plots (Table 4-1). Although capital costs were higher in the active and surface warming test plots, the rapid remediation time results in lower total costs for power and monitoring. Final costs based on \$/yd³ bioremediated illustrate that costs are comparable between the four treatment cells. These results indicate that implementation of a soil warming technology over basic bioventing is not necessarily based on cost, but on desired remediation time and funds available for operation and maintenance relative to capital costs.

Final soil sampling at this site was conducted in August 1994. Results of initial and final BTEX and TPH samples are shown in Figure 4-11 and 4-12, respectively. A dramatic reduction in BTEX was observed at all sample locations, while TPH on average was reduced by approximately 60%.

Spatial variability in contaminant distribution and biodegradation rates makes quantitative comparison between the test plots difficult; however, the results from the active, surface, and passive warming test plots clearly demonstrate that these forms of soil warming have increased biological activity in these areas. In the active and surface warming test plot, despite problems due to high soil

Table 4-1. Cost Analysis of Soil Warming Techniques at Site 20, Eielson AFB, Alaska¹

Task	Basic Bioventing (no warming)	Active Warming	Passive Warming	Surface Warming
Site Visit/Planning	5,000	5,000	5,000	5,000
Work Plan Preparation	6,000	6,000	6,000	6,000
Pilot Testing	27,000	27,000	27,000	27,000
Regulatory Approval	3,000	6,000	3,000	3,000
Full-Scale Construction				
Design	7,500	7,500	7,500	7,500
Drilling/Sampling	15,000	20,000 ²	15,000	15,000
Installation/Startup	4,000	26,000	10,500	13,000
Remediation Time Required³				
	9.4 years	2.8 years	6.9 years	3.4 years
Monitoring	30,550	9,800	24,150	11,050
Power	13,160	9,800	9,660	17,000
Final Soil Sampling	13,500	13,500	13,500	13,500
Cost per yd³	\$25.50	\$26.12	\$24.86	\$24.21

¹ Costs are estimated based on a 5,000-yd³ contaminated area with an initial contamination level of 4,000 mg/kg.

² Requires installation and development of one well.

³ Estimated based on average biodegradation rates in each test plot.

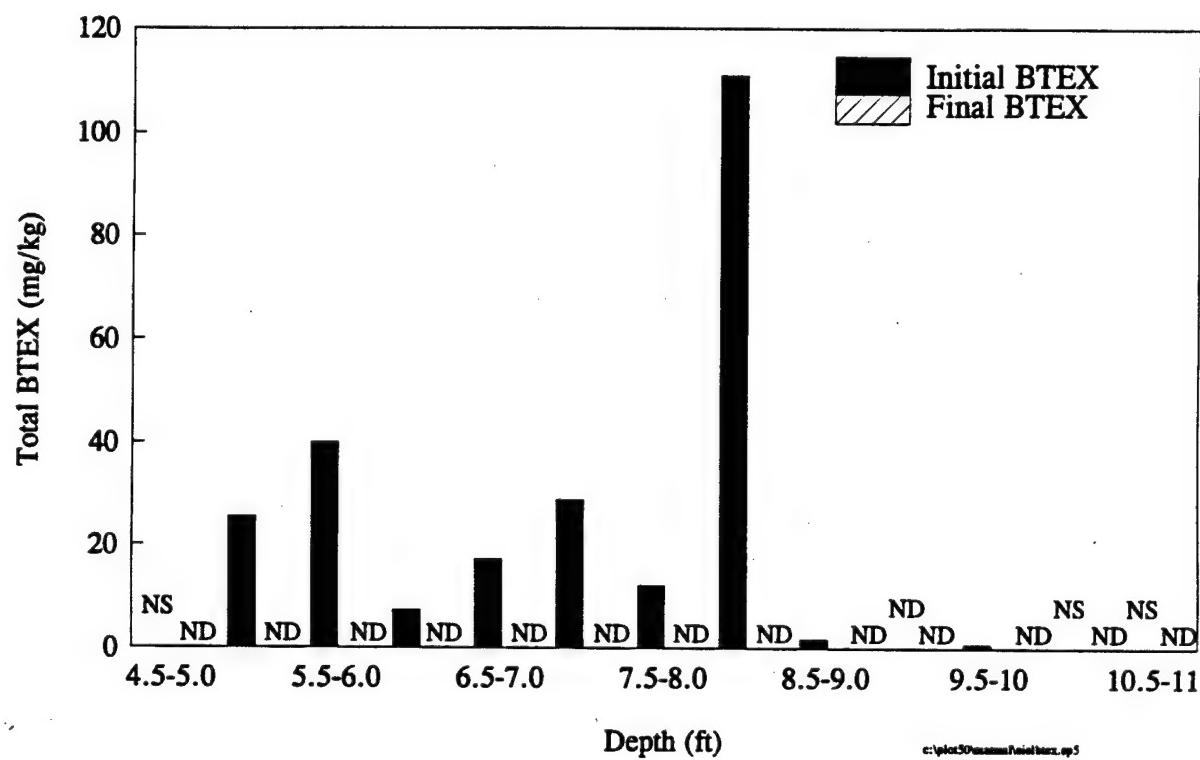


Figure 4-11. Site Average Initial and Final BTEX Soil Sample Results at Site 20, Eielson AFB, Alaska

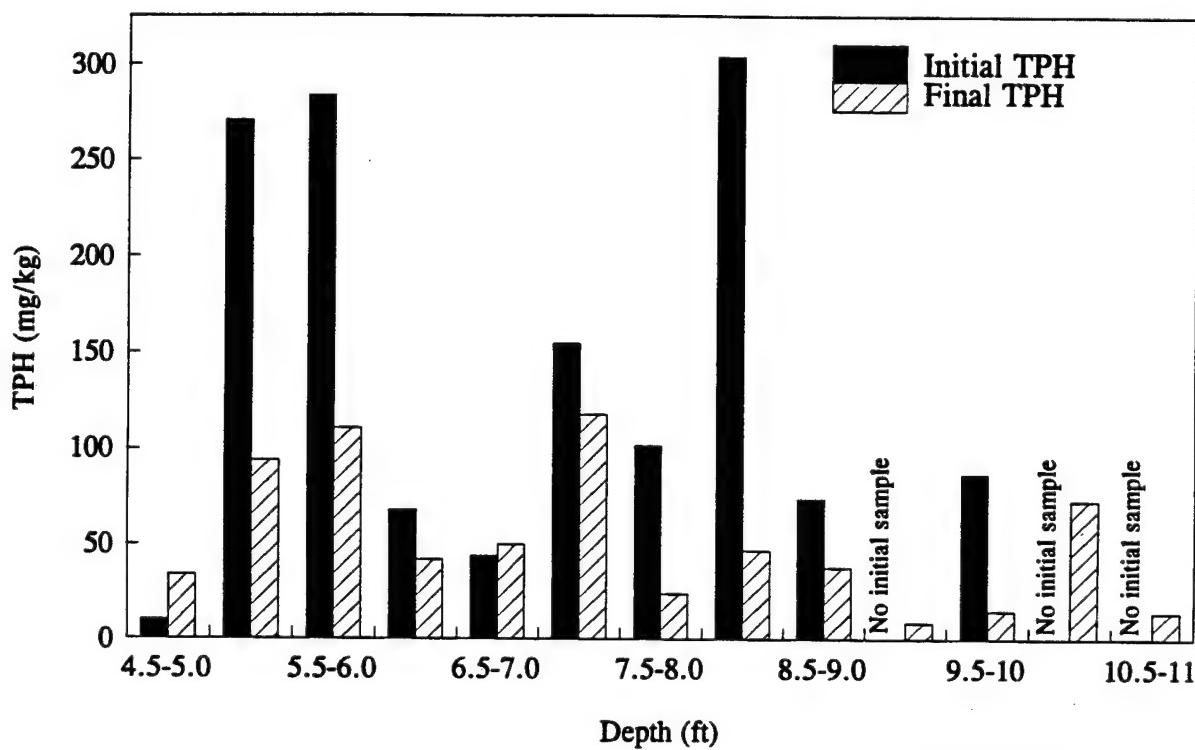


Figure 4-12. Site Average Initial and Final TPH Soil Sample Results at Site 20, Eielson AFB, Alaska

moisture content, biodegradation rates consistently have been higher than those measured in either the passive warming or the control test plot, even though the control test plot appears to be more heavily contaminated than the active warming test plot. These results have demonstrated the feasibility of bioventing in a subarctic climate and the potential advantages of soil warming to accelerate remediation.

Further details of the Site 20, Eielson AFB study may be found in Leeson et al. (1995) and Sayles et al. (1994a).

4.5 Fire Training Area, Battle Creek ANGB, Michigan

The Fire Training Area, Battle Creek ANGB, was included as part of the Bioventing Initiative. It was estimated that approximately 54,000 to 74,000 gallons of mixed waste fuels, oils, and solvents were burned at this site during fire training exercises. Soils at the site consist of fine to coarse silty sand interbedded with gravel and cobbles (Figure 4-13). Groundwater is at a depth of approximately 30 ft.

As dictated by the Bioventing Initiative protocol, one vent well and three monitoring points were installed at this site. The vent well was installed to a depth of 30 ft with 20 ft of 0.04-inch slotted screen. The monitoring points were three-level, with screens located at depths of 8, 17, and 27 ft and were located at distances of 15, 30, and 50 ft away from the vent well.

Initial treatability tests — an in situ respiration test and a soil gas permeability test — were conducted to determine the feasibility of bioventing. Oxygen utilization rates ranged from 2.9 to 22 %/day (2.0 to 15 mg/kg-day), with higher rates associated with more contaminated locations. Soil gas permeability testing demonstrated an average permeability of approximately 230 darcys and a radius of influence of greater than 50 ft. These results indicated that both the microbial activity and the permeability were conducive to an effective bioventing operation.

Initial soil and soil gas samples were collected and a 1-hp regenerative blower was installed at the site for continuous air injection in September 1992. The blower was operated for 1 year and in October 1993, final soil and soil gas samples¹ were collected. Although the number of soil and soil gas samples collected was not sufficient to allow for statistically significant comparison of the data,

¹ Blower operation was discontinued for 1 month prior to collecting soil gas samples to allow time for soil gas equilibration.

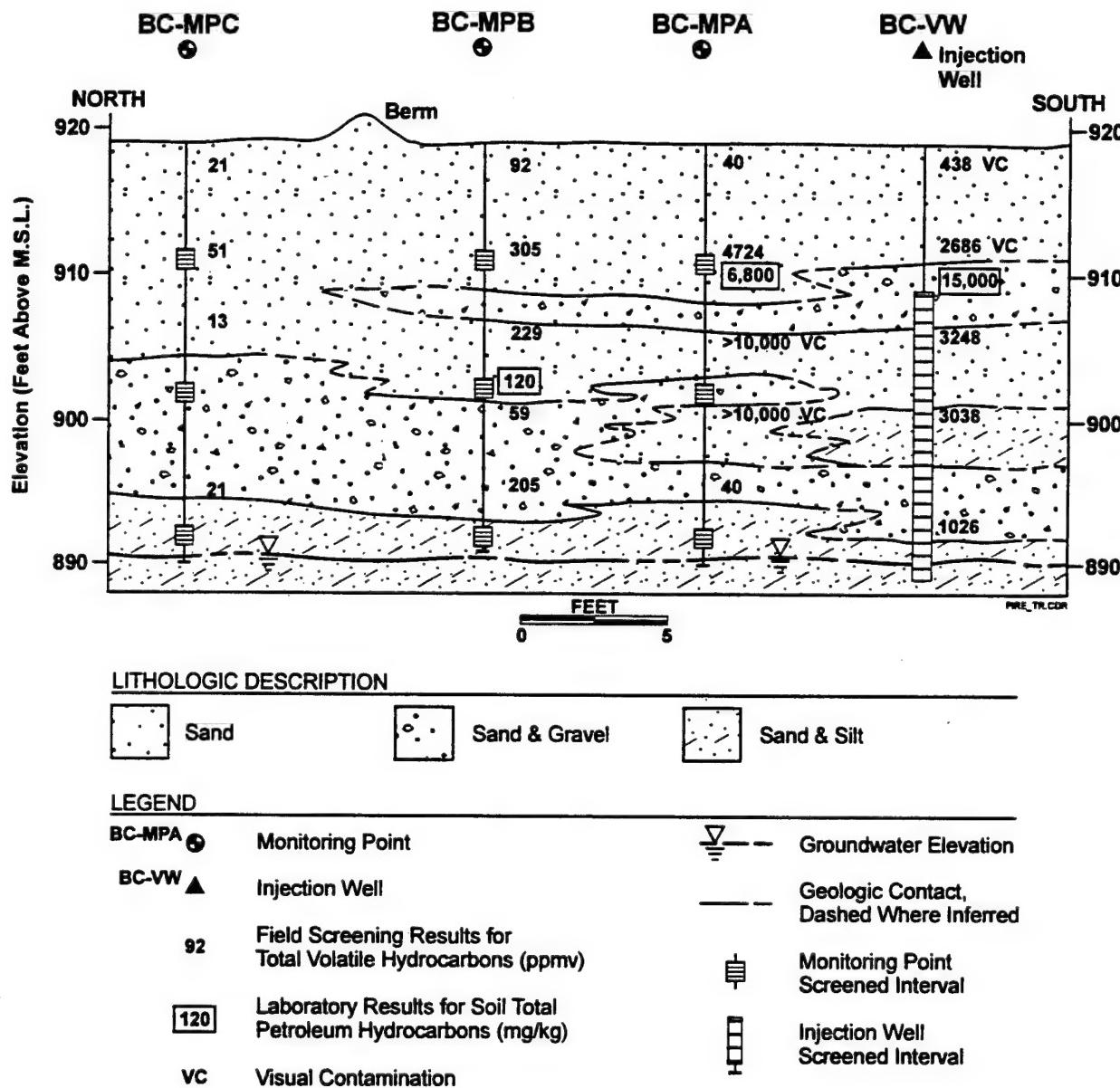


Figure 4-13. Hydrogeologic Cross Section of the Fire Training Area, Battle Creek ANGB, Michigan (Engineering-Science, 1992)

certain trends were observed¹. Final BTEX and TPH soil gas concentrations were significantly lower than the concentrations measured initially (Figure 4-14). Soil BTEX concentrations were significantly lower after 1 year of bioventing, whereas soil TPH concentrations changed little, as expected (Figure 4-15). In addition, in situ respiration rates declined from rates in the initial treatability test, which is an indication of decreased contaminant levels². These results illustrate the effectiveness of bioventing at this site. Because Michigan uses a risk-based standard for site closure, the Battle Creek site is likely to be closed based on these results.

Further details of the Fire Training Area, Battle Creek ANGB study may be found in Engineering-Science (1992).

¹ Three initial soil samples were collected, but 29 final soil samples were collected as part of an intrinsic remediation study.

² Refer to Section 4.0, Volume II for a detailed discussion of in situ respiration rates and site closure.

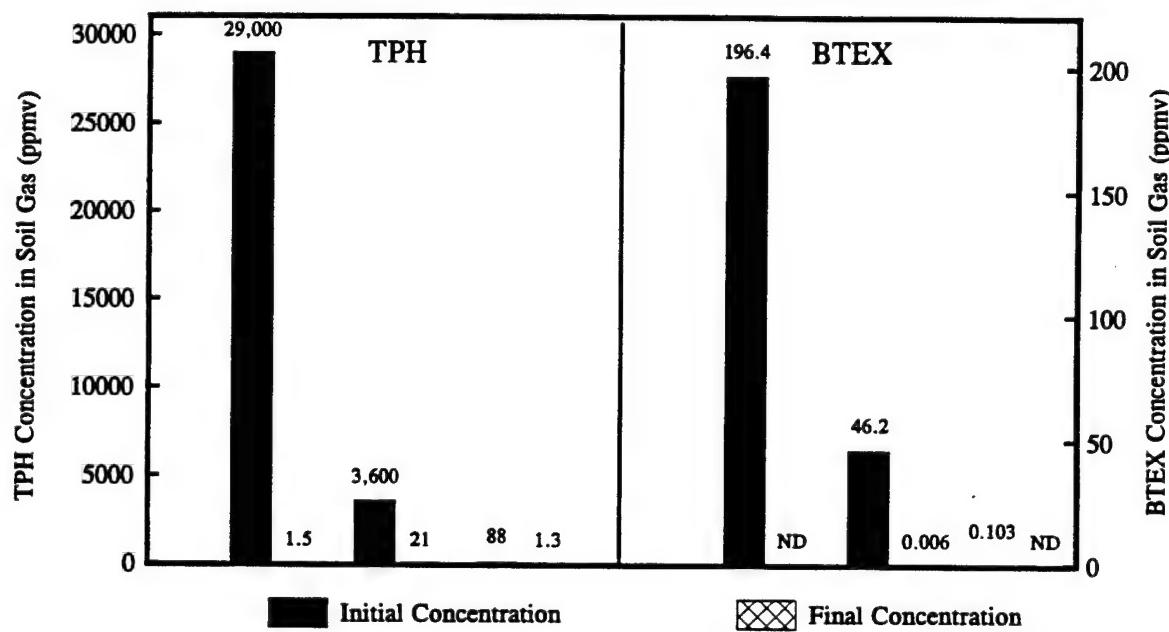


Figure 4-14. Initial and Final Soil Gas Concentrations at the Fire Training Area, Battle Creek, Michigan

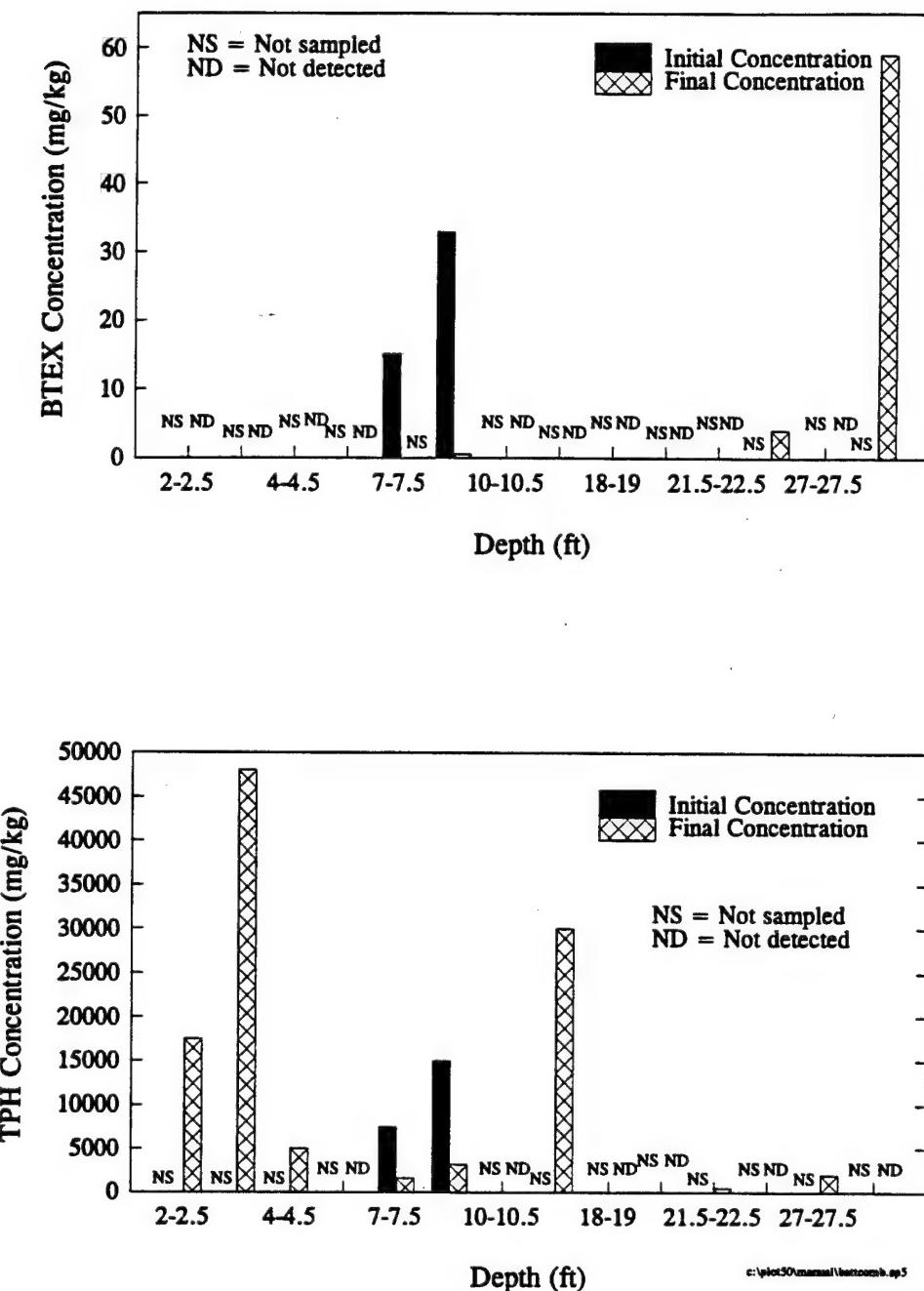


Figure 4-15. Initial and Final Soil Concentrations at the Fire Training Area, Battle Creek, Michigan

5.0 ANALYSES OF BIOVENTING INITIATIVE RESULTS

In May 1992, the U.S. Air Force began the Bioventing Initiative to examine bioventing at 55 contaminated sites throughout the country. In December 1992, the program was increased to more than 130 sites due to increased demand by Air Force managers. To date, data have been collected from 125 contaminated sites at a total of 50 Air Force bases, one Army base, one Naval installation, and one Department of Transportation installation. Sites are located in 35 states and in all 10 U.S. EPA regions. Figure 2-2 illustrates the locations of Bioventing Initiative sites to date. The selected sites represent a wide range of contaminant types and concentrations, soil types, contaminant depths, climatic conditions, and regulatory frameworks. Sites were selected based on contamination level (preferably $> 1,000 \text{ mg/kg TPH}$). The selections were not biased with regard to factors such as soil type or climatic conditions, in order to properly evaluate bioventing potential under both favorable and unfavorable conditions.

A Bioventing Test Protocol was developed which provided strict guidelines for treatability testing and bioventing system design. The Bioventing Test Protocol was peer reviewed and was reviewed by U.S. EPA Headquarters and the U.S. EPA National Risk Management Research Laboratory. Using the Bioventing Test Protocol, initial testing was conducted at each site to determine whether bioventing was feasible. Based on the initial testing, a decision was made whether to install a bioventing system for 1 year of operation. At the majority of sites (95%), a bioventing system was installed for the 1-year operational period. At the end of this time period, each Air Force base could either elect to keep the bioventing system in operation or remove it if the site were deemed to have been remediated sufficiently.

At each site in which a bioventing system was installed, a series of data was collected as described in Section 2.3: initial site characterization data consisting of soil and soil gas sampling, in situ respiration rate testing results, and soil gas permeability testing results; 6-month in situ respiration testing results; and 1-year soil and soil gas sampling and in situ respiration testing results. Data from the initial testing are summarized in Appendix B and have been used in the statistical analyses as described in Section 5.2. A summary of the results to date with potential implications is presented in the following sections.

5.1 Estimate of Contaminant Removal at Bioventing Initiative Sites

At all Bioventing Initiative sites in which a blower was installed and operated for 1 year, initial and final soil and soil gas BTEX and TPH concentrations were measured. The approach was to compile a limited number of samples from each site and statistically analyze for trends to avoid known spatial variability. Distributions of soil and soil gas BTEX and TPH concentrations from the initial and 1-year sampling events are shown in Figures 5-1 through 5-4, respectively. The average soil and soil gas BTEX and TPH concentrations across all sites are shown in Figure 5-5. In general, the most dramatic reductions were observed in BTEX removal in both soil and soil gas samples. As an example, soil results from Site 3 at Battle Creek ANGB are shown in Figure 5-6. After 1-year of bioventing operation the BTEX concentrations are very low and are no longer a source of groundwater contamination; therefore, site closure is now a viable option for this site.

The objective of the 1-year sampling event was not to collect the large number of samples required for statistical significance for a single site. Rather, the objective was to give a qualitative indication of changes in contaminant mass. Soil gas samples are somewhat similar to composite samples in that they are collected over a wide area. Thus, they provide an indication of changes in soil gas profiles (Downey and Hall, 1994). Blower operation was discontinued 30 days prior to sample collection to allow for soil gas equilibration. In contrast, soil samples are discrete point samples subject to large variabilities over small distances/soil types. Given this variability, coupled with known sampling and analytical variabilities, a large number of samples at a single site would have to be collected to conclusively determine real changes in soil contamination. Due to the limited number of samples, these results should not be viewed as conclusive indicators of bioventing progress or evidence of the success or failure of this technology.

If a risk-based approach to remediation is used which focuses on removing the soluble, mobile, and more toxic BTEX component of the fuel, remediation times can be significantly reduced. As discussed in the Tyndall AFB case history¹, the BTEX fraction was removed preferentially over TPH. The potential for bioventing to preferentially remove BTEX makes this technology suitable for risk-based remediations. In addition, the low levels of BTEX that have been encountered at the

¹ Refer to Section 4.2 for a presentation of this case history.

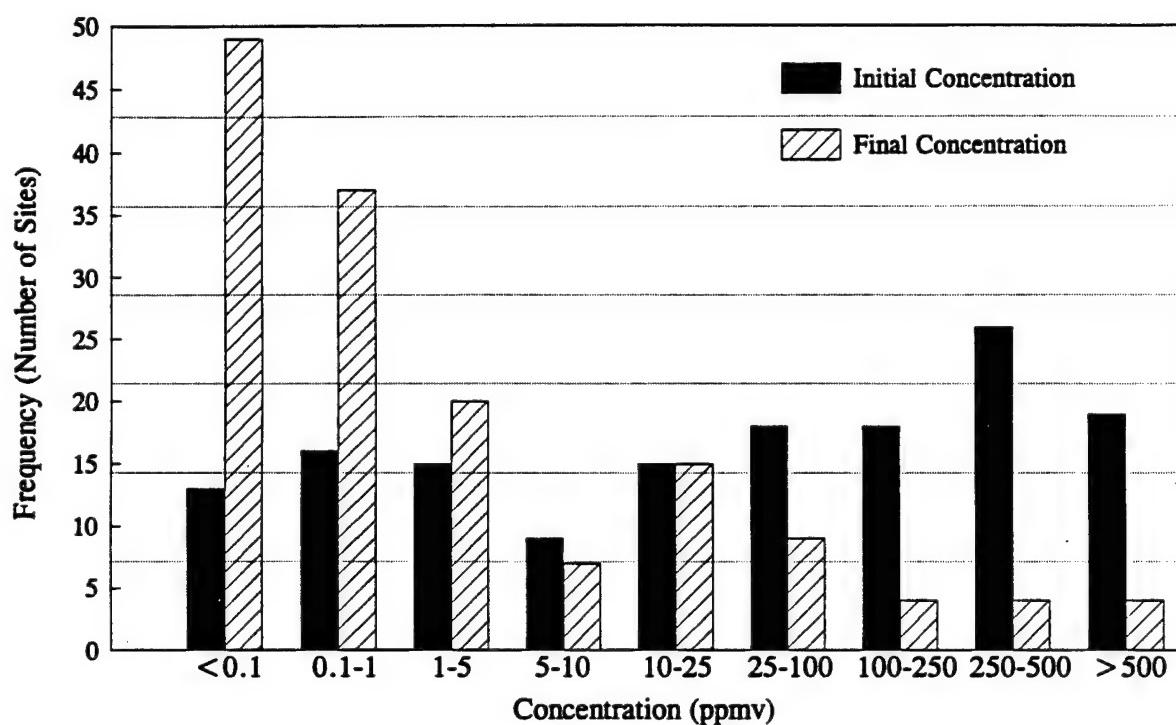


Figure 5-1. Soil Gas BTEX Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data

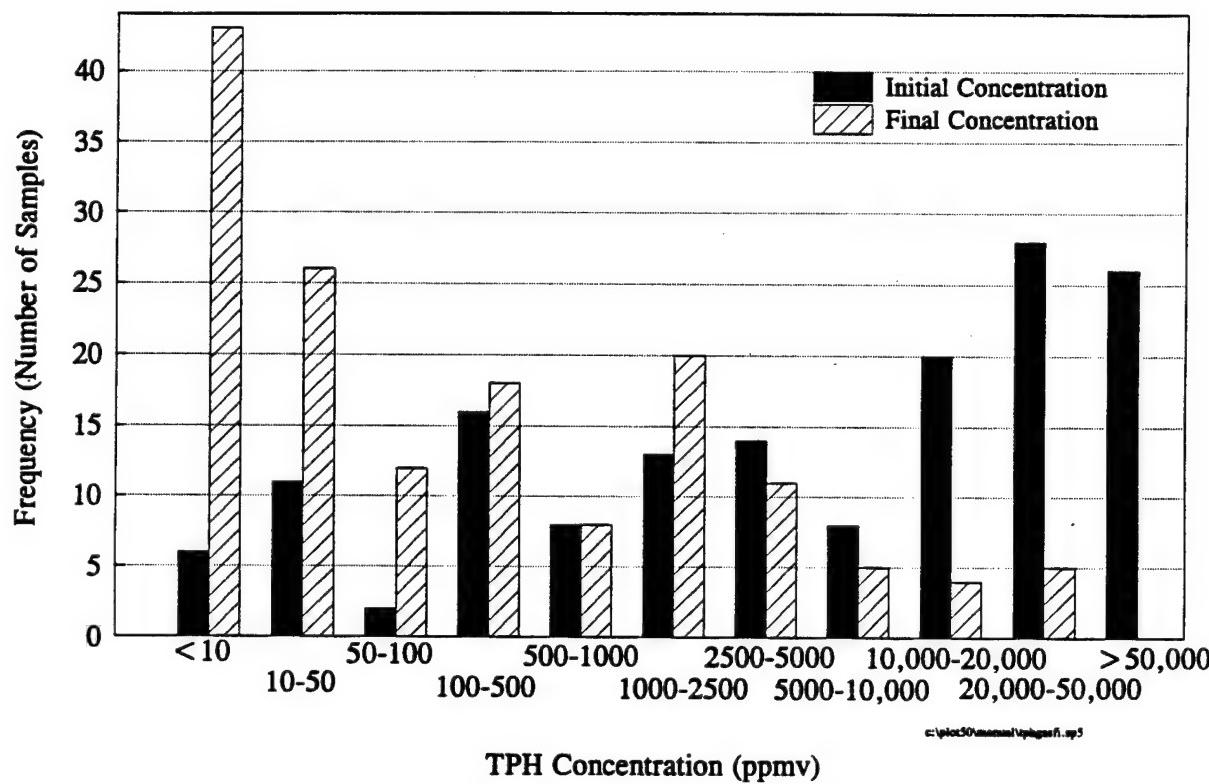


Figure 5-2. Soil Gas TPH Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data

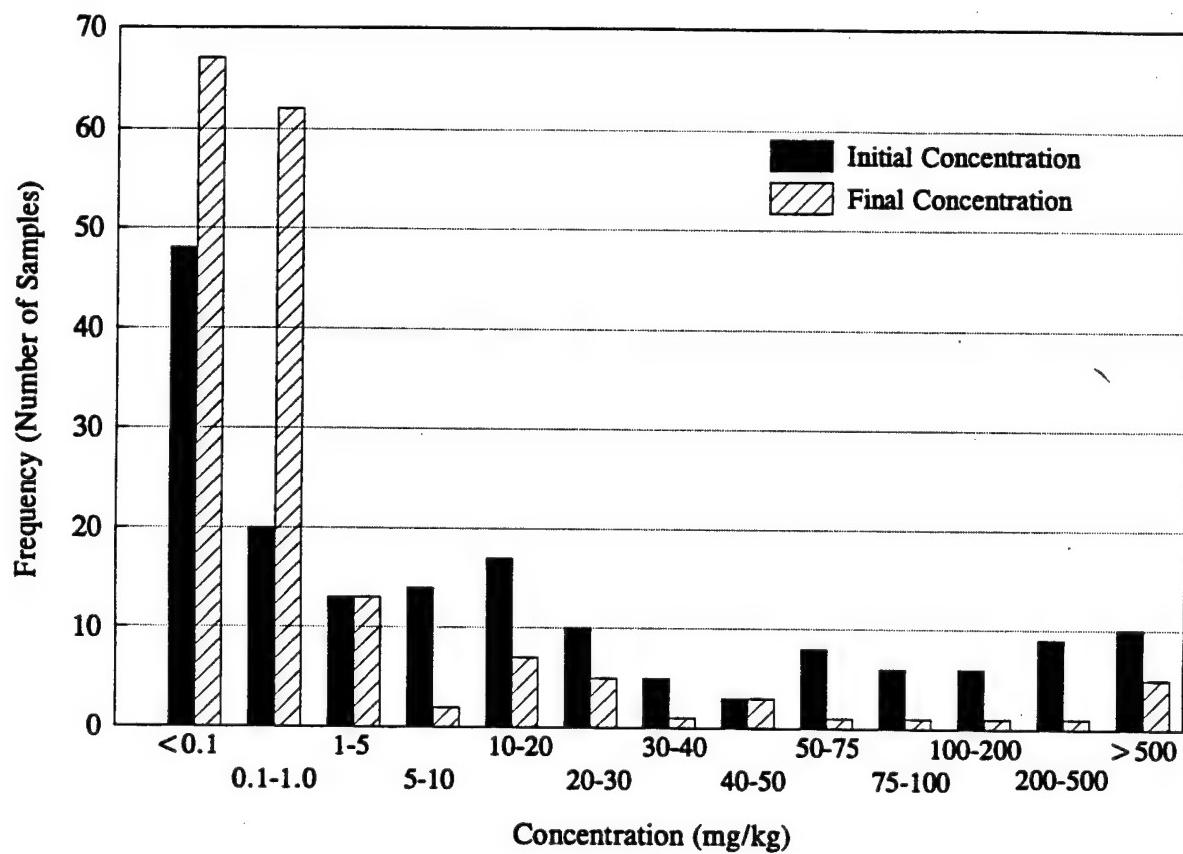


Figure 5-3. Soil BTEX Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data

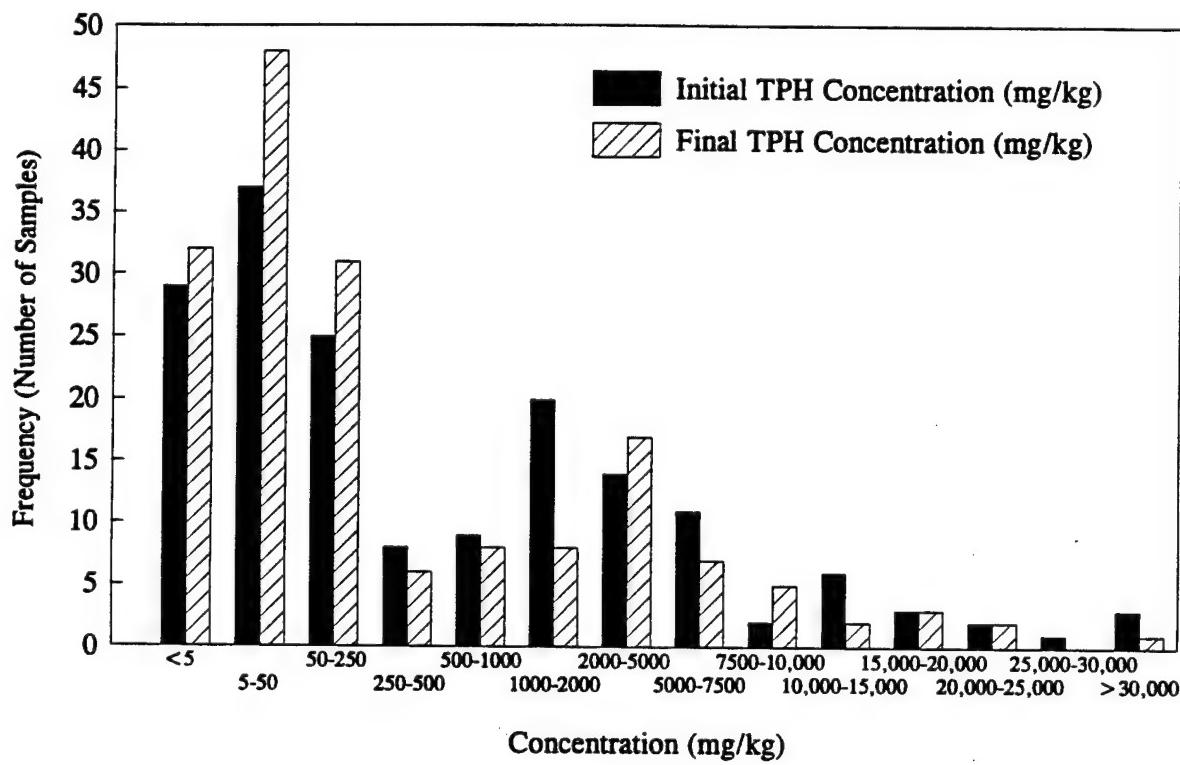


Figure 5-4. Soil TPH Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data

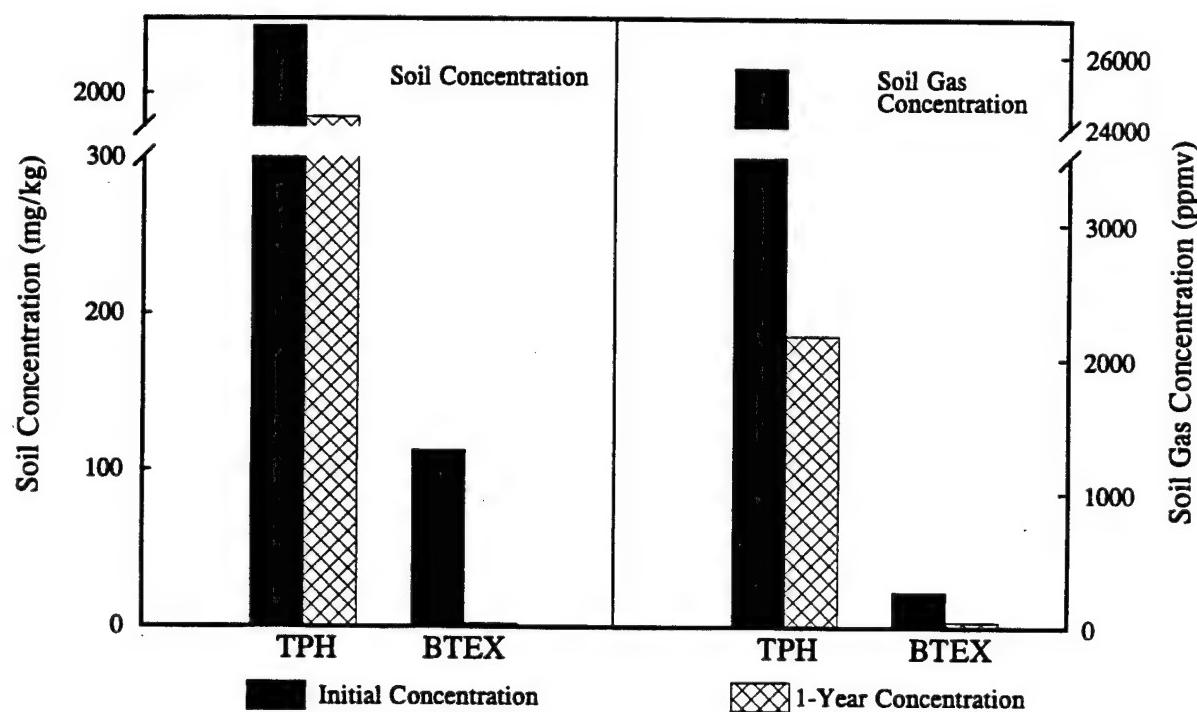


Figure 5-5. Average Soil and Soil Gas BTEX and TPH Concentrations at Bioventing Initiative Sites: Initial and 1-Year Data

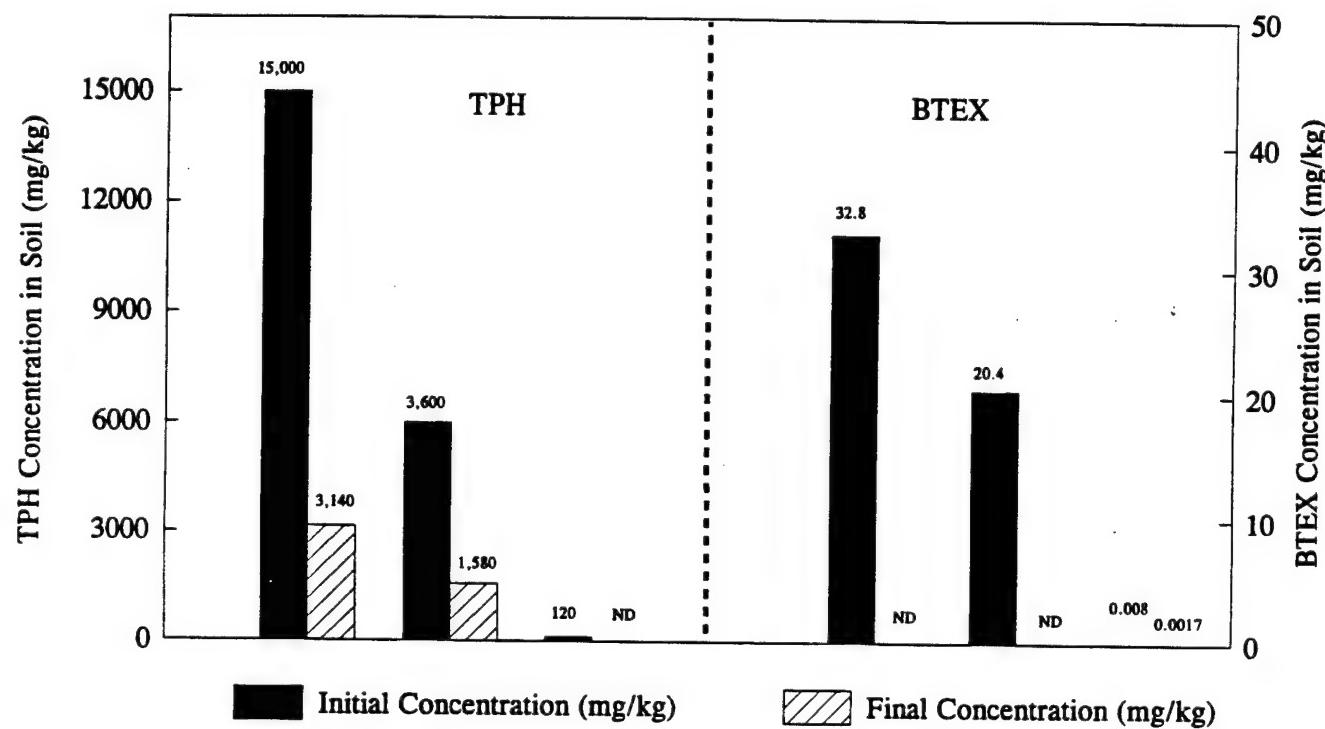


Figure 5-6. Initial and Final Soil Sampling Results at Site 3, Battle Creek ANGB, Michigan

majority of the Bioventing Initiative sites further support an emphasis on risk-based remediation (Figure 5-7). Over 85% of the initial soil samples contained less than 1 mg/kg of benzene.

5.2 Statistical Analysis of Bioventing Initiative Data

One of the primary objectives of the Bioventing Initiative was to develop a large database of bioventing systems from which it could be determined which parameters are most important in evaluating whether to implement bioventing. This effort is the largest field effort to date where data have been collected in a consistent manner to allow for direct comparison of results across sites. Results of the statistical analyses can be used to evaluate which soil measurements should be taken and, if bioventing performance is poor, which parameters may be adjusted to improve performance.

Data generated from the Bioventing Initiative were subjected to thorough statistical analyses to determine which parameters most influenced observed oxygen utilization rates. Procedures used for conducting the statistical analyses and the results of these analyses are presented in the following sections.

5.2.1 Procedures for Statistical Analysis

Data collected from 125 Bioventing Initiative sites have been analyzed for this study. The study involved *in situ* respiration test data, soil gas permeability test data, and soil chemistry and nutrient data from each site. Several parameters were measured in the soil samples. The statistical analyses had five specific objectives:

- To develop a consistent statistical approach for calculating the oxygen utilization and carbon dioxide production rates from the *in situ* respiration data.
- To characterize the oxygen utilization rate as a function of parameters measured during initial testing.
- To determine the relationship between carbon dioxide production rate and pH or alkalinity by characterizing the ratio of oxygen utilization rate to carbon dioxide production rate as a function primarily of pH and alkalinity.

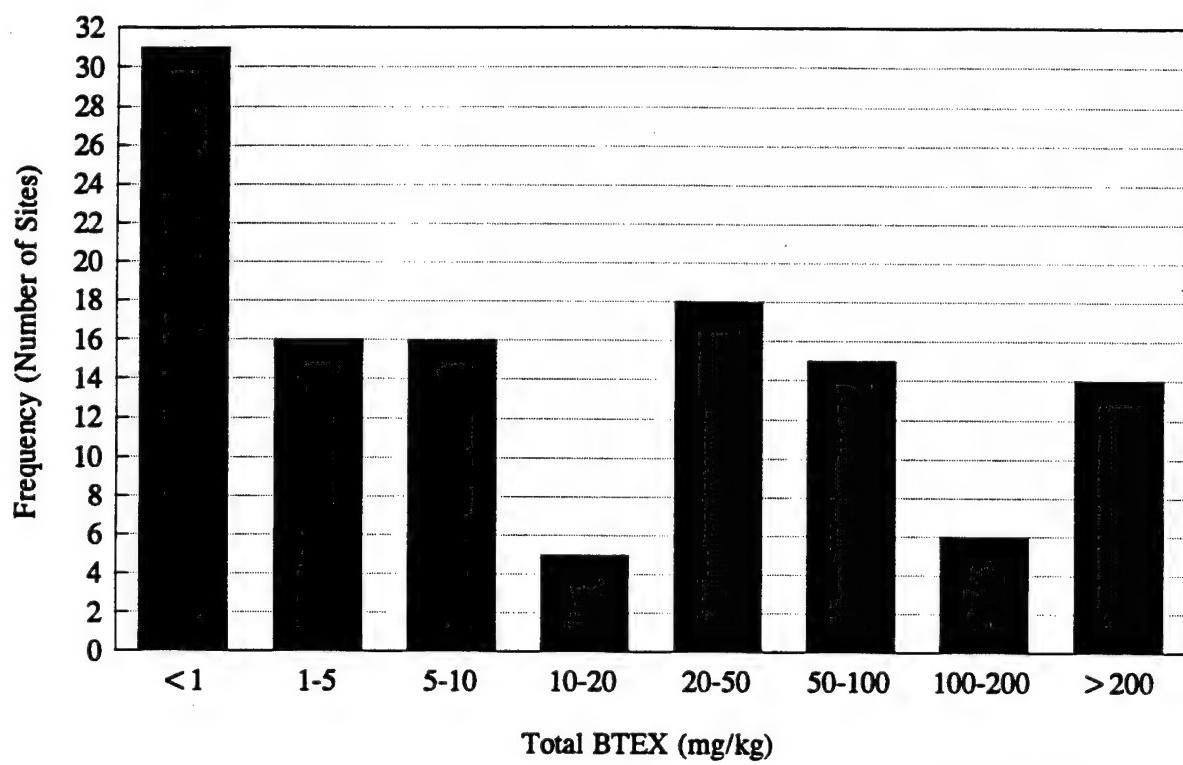


Figure 5-7. Average BTEX Concentrations at Bioventing Initiative Sites

- To characterize soil gas permeability as a function of particle size and moisture content.
- To compare TKN concentrations at contaminated sites with those at uncontaminated background areas.

Averages for oxygen utilization and carbon dioxide production rates and soil parameters were computed for each site. All subsequent analyses were performed on the site averages. Table 5-1 displays the parameters included in the statistical analyses, their units, and transformations performed on these parameters whenever necessary.

Data were stored in Statistical Analysis System (SAS) databases and all statistical manipulations and analyses were conducted using the SAS software package. Methods used for characterizing the data and the final regression model are presented in the following sections for each of the listed objectives.

5.2.2 Calculation of Oxygen Utilization and Carbon Dioxide Production Rates

A statistical analysis was conducted to consistently calculate oxygen utilization and carbon dioxide production rates. A linear, time-related change in oxygen and carbon dioxide levels that is characterized by a constant (or zero-order) rate is typical of most of the sites. However, in some sites, a two-piecewise linear change is observed. An initial rapid rate is observed followed by a leveling off. This change in rates generally occurs once oxygen becomes limiting, typically below 5 to 10% oxygen.

The two-piecewise regression model, with a slope change at time t_0 , was fitted to the oxygen (and carbon dioxide) versus time data obtained at every monitoring point. The piecewise regression model is presented below:

$$R_i = \alpha + \beta t_i \quad t_i \leq t_0 \quad (5-1)$$

$$R_i = (\alpha + \beta t_0) + (\beta + \delta) (t_i - t_0) \quad t_i > t_0 \quad (5-2)$$

for $i = 1, 2, \dots, \#$ of observations at each monitoring point, and where:

Table 5-1. Data Parameters Included in the Statistical Analyses

Category	Parameter	Units	Transformation ^a	Acronym ^b
In Situ Respiration Rates	Oxygen utilization rate	%/hr	Log	O2
	Carbon dioxide production rate	%/hr	None	CO2
	Ratio of the carbon dioxide production rate to oxygen utilization rate	No units	Square root	Ratio
Soil Parameters	Soil gas TPH	ppmv	Log	tphsg
	Soil gas BTEX	ppmv	Log	btxsg
	Soil TPH	mg/kg	Log	tphs
	Soil BTEX	mg/kg	Log	btxs
	pH	No units	Log	PH
	Alkalinity	mg/kg as CaCO ₃	Log	ALK
	Iron content	mg/kg	Log	IRN
	Nitrogen content	mg/kg	Log	NIT
	Phosphorus content	mg/kg	Log	PHO
	Moisture content	% wt	None	MOI
	Gravel	% wt	None	GRA
	Sand	% wt	None	SAN
	Silt	% wt	None	SIL
	Clay ^c	% wt	None and log	CLA
Other	Soil gas permeability	Darcy	Log	PRM
	Soil temperature	Celsius	None	TMP
Other	Season (time of year)	Day	None	season

a Transformation was applied to the parameter for purposes of statistical analysis.

b Acronym is used for the parameter in this report.

c The correlations in Figures 5-9 through 5-14 and Figure 5-17 are based on untransformed clay.

- R_i = measured i^{th} oxygen or carbon dioxide level at time t_i (%);
 α = oxygen or carbon dioxide level at initial time (%);
 β = rate of change of oxygen or carbon dioxide level with time (%/hr);
 δ = increase or decrease in the rate of change at time t_0 (%/hr);
 t_0 = time at which the slope change occurs (hr).

The piecewise regression model was implemented using the NLIN procedure (nonlinear regression procedure) in the SAS software package.

The parameter δ in the above model measures the increase or decrease in the slope at time t_0 . Therefore, the statistical significance of δ confirmed the suitability of a two-piecewise model fitted to the data. The rate of oxygen utilization (or carbon dioxide production) was estimated from the slope of the first linear piece, β , whenever δ was statistically significant at the 0.05 significance level. For example, Figure 5-8 presents the piecewise linear model fitted to oxygen data at a monitoring point at Site FSA-1, Air Force Plant (AFP) 4, Texas, where β was estimated to be $-1.1\text{ \%}/\text{hr}$.

In cases where δ was not significant at the 0.05 level, a linear regression model of the following form was fitted to the data:

$$R_i = \alpha + \beta t_i \quad \text{for all } t_i \quad (5-3)$$

where: the rate of oxygen utilization (or carbon dioxide production) was determined from the slope of the straight line, β .

For cases in which six or fewer observations were available at a monitoring point, or when the oxygen levels exhibited virtually no change over a short initial time period followed by a linear change, the piecewise analysis was not attempted. In such cases, a linear regression model, as described above, was fitted. In these cases, the suitability of the linear model was confirmed by inspection of the model-fit to observed data.

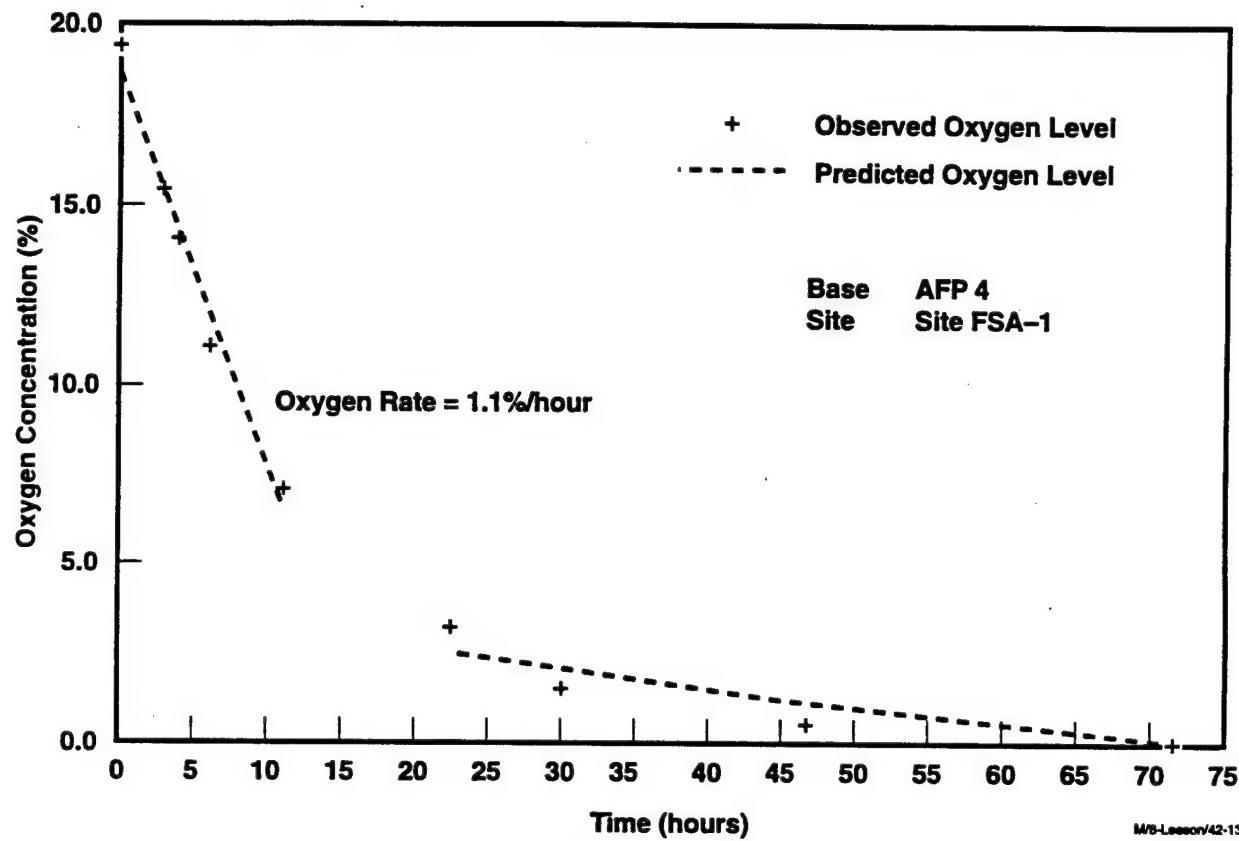


Figure 5-8. Use of Piecewise Analysis of Oxygen Utilization Data from Site FSA-1, AFP 4, Texas

5.2.3 Correlation of Oxygen Utilization Rates and Environmental Parameters

A preliminary analysis of the untransformed data was performed in which a regression model was fitted to the oxygen utilization rate using forward stepwise regression. This model accounted for the effects of the soil parameters and their interactions. In order to reduce the effect of multicollinearity among the parameters on the fitted model, soil gas BTEX levels and gravel were excluded from the modeling. In other words, soil gas BTEX was highly correlated with soil gas TPH, and therefore it was concluded that the effect of soil gas BTEX levels on the oxygen utilization rate can almost completely be explained by soil gas TPH concentrations. Also, since the particle size levels added up to a constant value (100%), the effect of gravel was assumed to be redundant in the modeling.

As a result of fitting the regression model to the oxygen utilization rate it was found that soil particle sizes and permeability had a dominating influence on the oxygen utilization rate; that is, low levels of permeability and sand, and high levels of silt and clay appeared to correlate strongly with high oxygen utilization rates.

In order to determine whether a handful of sites were unduly influencing the statistical modeling, sites with high oxygen utilization rates were examined in detail. Seven sites in the analyses had extremely high oxygen utilization rates, well above average rates from other sites. A two-sample t-test was performed on each parameter (e.g. sand, nitrogen, etc.) to determine whether the average value of the parameter over the seven sites was different from the corresponding average for the remaining sites. This analysis revealed statistically significant differences in particle size, soil gas permeability, and soil TPH concentrations between the two groups of sites (Table 5-2). As a result of this analysis, it was determined that the seven sites with extremely high oxygen utilization rates were atypical with respect to their levels of particle size, soil gas permeability, and soil TPH concentrations.

In order to reduce the influence on the model for the oxygen utilization rate caused by these seven sites, the log transformation of the oxygen utilization rate was taken. Additionally, the log transform resulted in more normally distributed data for the oxygen utilization rate. However, sites with oxygen utilization rates near zero receive artificial importance as a result of the transformation. To eliminate this artificial effect caused by the log-transformation, all the log-transformed values of

Table 5-2. Parameters That Distinguish the Seven Sites with High Oxygen Utilization Rates From the Remaining Sites

Parameter	Level of Parameter in Seven Sites Relative to Other Sites
Sand	Lower
Silt	Higher
Clay	Higher
Soil Gas Permeability	Lower
Soil TPH	Lower

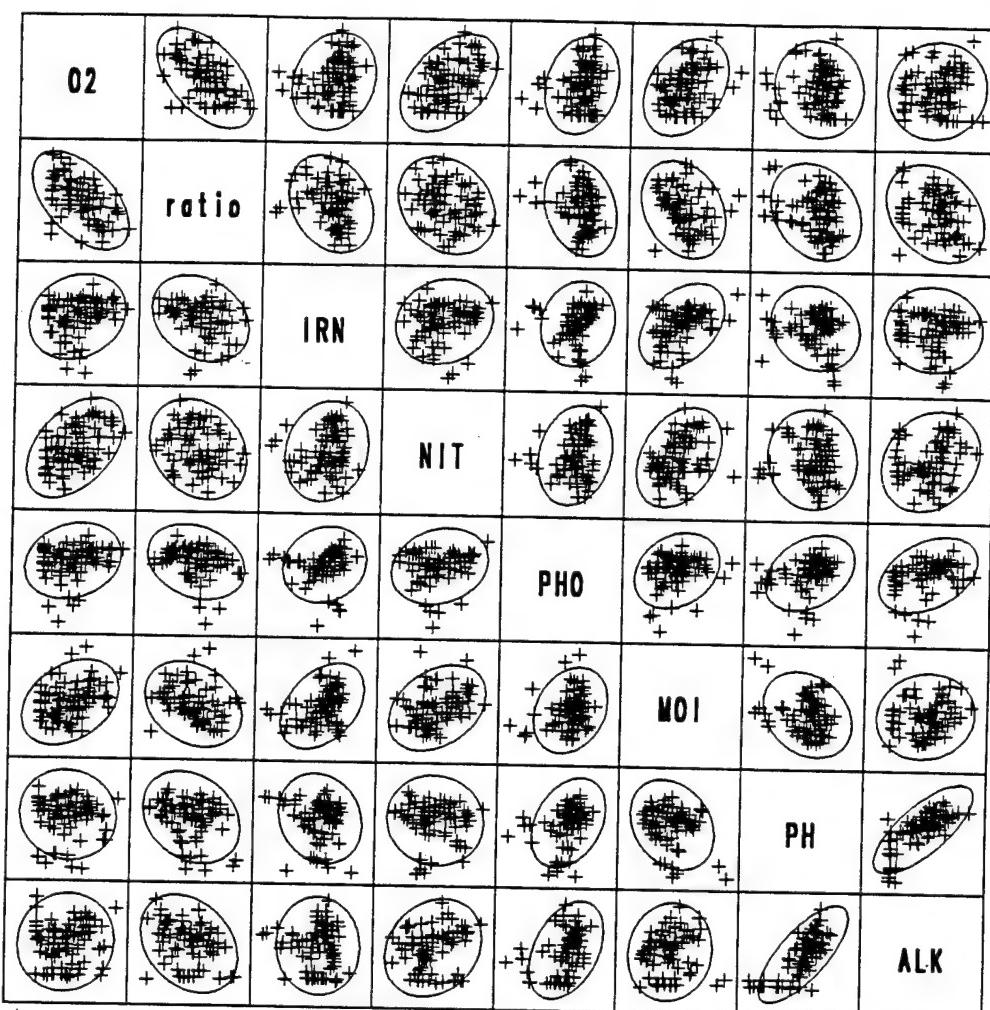
the oxygen utilization rate below -2.5 were censored, that is, set to a constant value of -2.5.

Censoring was based on visual inspection of the log-transformed data.

Subsequently, the log transform of some of the soil parameters was taken if the data for the parameter were not well represented by a normal distribution. Normality in the data was checked using the Shapiro-Wilk test for normality and by observing histograms and normal probability plots.

As a preliminary step to determine the influence of the soil parameters on the oxygen utilization rate, correlations between the rate and each of the soil parameters were examined. This step was conducted to examine strong relationships between oxygen utilization rates and measured environmental parameters to assist in developing a statistical model describing performance at the Bioventing Initiative sites. First, the log transformation of the oxygen utilization rate and some of the soil parameters was taken to obtain more normally distributed data on each parameter (Table 5-1). After these transformations, the data for each parameter were plotted against the corresponding data for each of the other parameters.

Figures 5-9 through 5-14 display the magnitude of the correlations among the data parameters. Specifically, Figures 5-9 through 5-11, display the correlations between the oxygen utilization rate and the soil parameters and Figures 5-12 through 5-14 present the correlations between the soil parameters. In each of these figures, ellipses are drawn on each plot containing 95% of the estimated bivariate distribution. The plots for which the ellipses are narrow represent pairs of elements that have a strong observed correlation. Pairs of elements that are positively correlated have the ellipse with the major axis running from the lower-left to the upper-right, whereas negative correlations are indicated by the major axis running from the lower-right to the upper-left. The

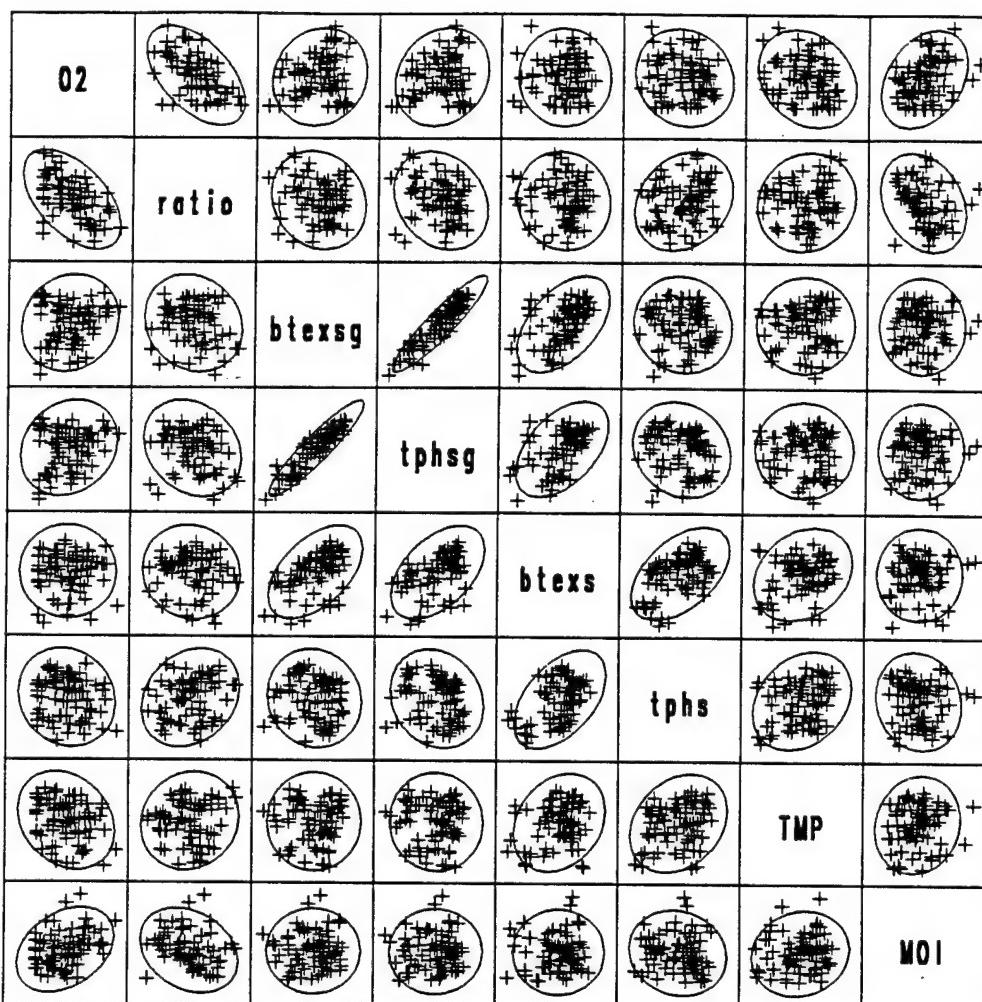


$O_2 = \log O_2 \text{ Rate}$ $\text{Ratio} = (\text{CO}_2 \text{ Rate}/O_2 \text{ Rate})^x$ $IRN = \log \text{Iron}$ $NIT = \log \text{Nitrogen}$
 $PHO = \log \text{Phosphorus}$ $MOI = \text{Moisture}$ $PH = \log \text{pH}$ $ALK = \log \text{Alkalinity}$

	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

Figure 5-9. Oxygen Utilization Rates, Oxygen:Carbon Dioxide Rate Ratios, Element Concentrations, Moisture Content, pH, and Alkalinity Site Average Correlation Scatterplot

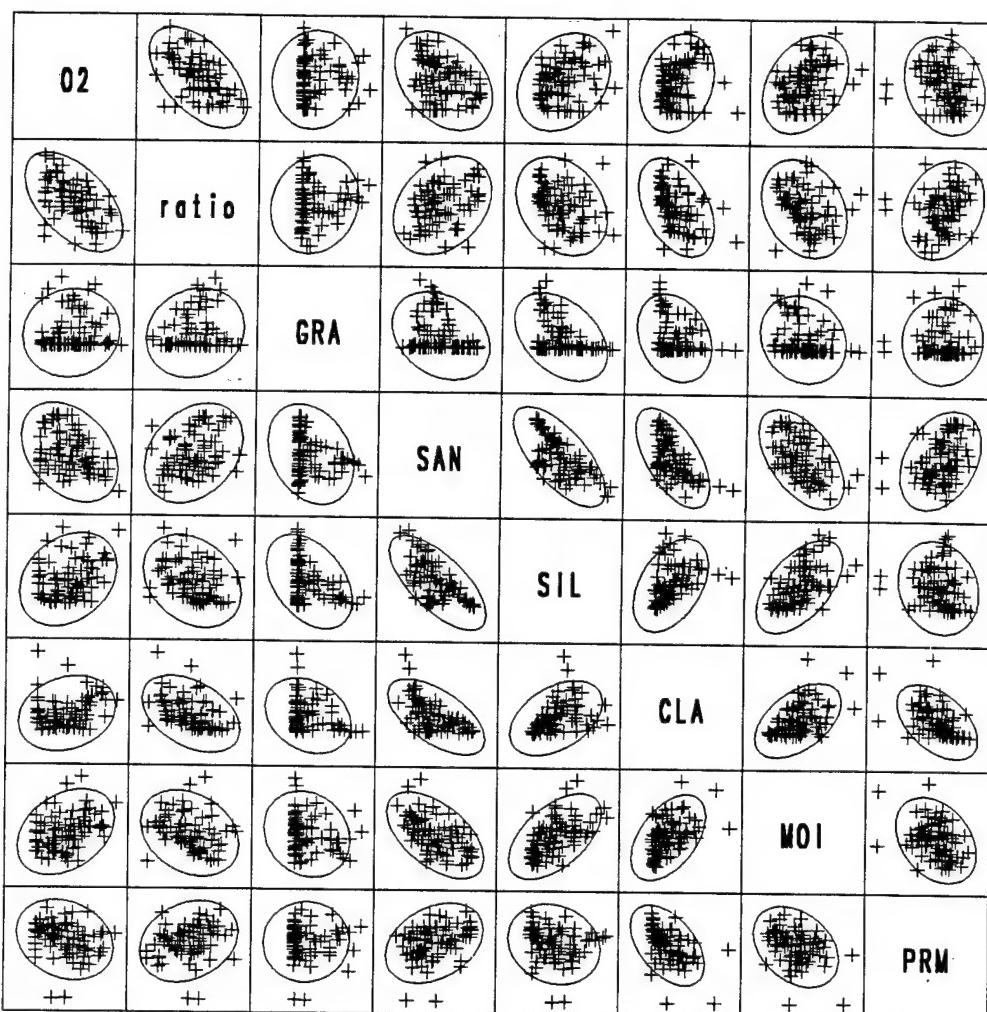


O_2 = log O_2 Rate Ratio = $(CO_2 \text{ Rate}/O_2 \text{ Rate})^n$ btexsg = log BTEX in Soil Gas tphsg = log TPH in Soil Gas
 btxs = log BTEX in Soil tphs = log TPH in Soil TMP = Soil Temperature MOI = Moisture

	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

Figure 5-10. Oxygen Utilization Rates, Oxygen:Carbon Dioxide Rate Ratios, Contaminant Concentrations, Temperature, and Moisture Content Site Average Correlation Scatterplot

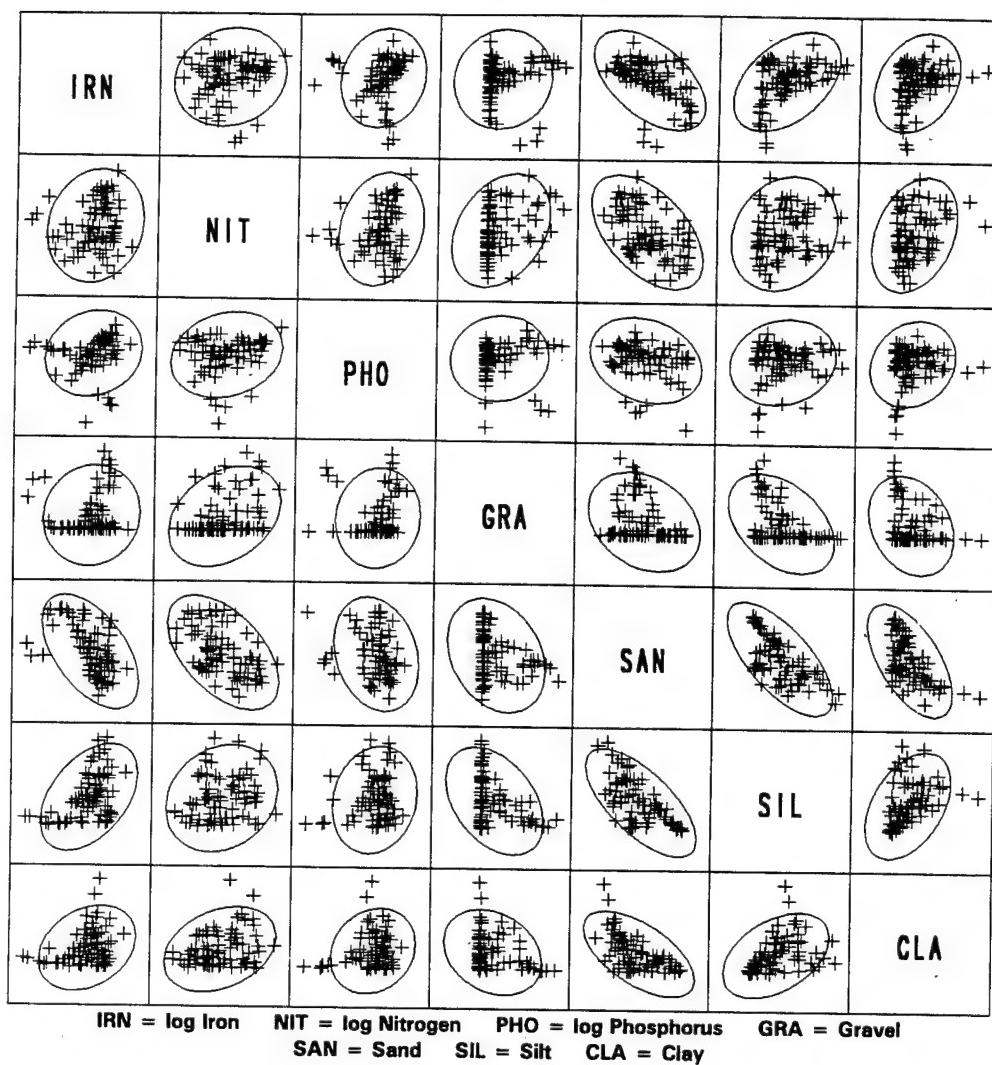


$O_2 = \log O_2$ Rate Ratio = $(CO_2$ Rate/ O_2 Rate) n GRA = Gravel SAN = Sand SIL = Silt
 CLA = Clay MOI = Moisture PRM = \log Soil Gas Permeability

	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

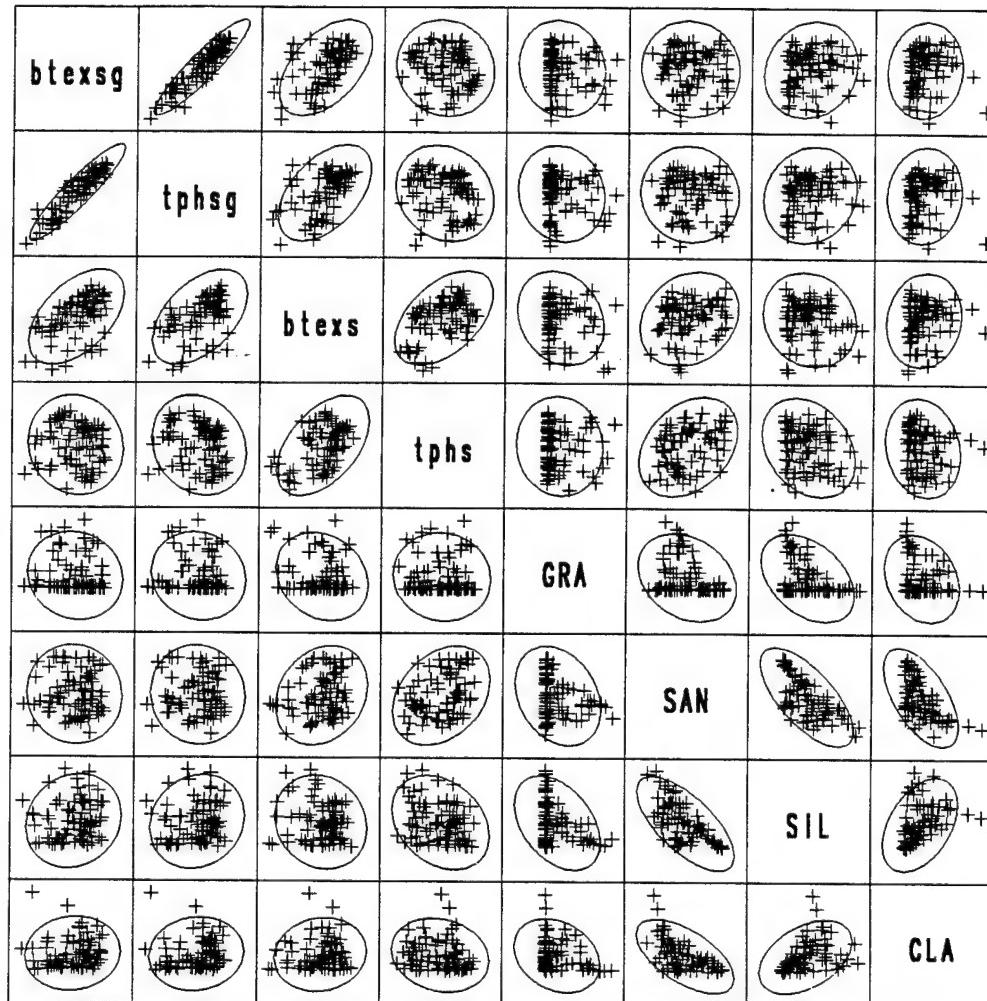
Figure 5-11. Oxygen Utilization Rates, Oxygen:Carbon Dioxide Rate Ratios, Particle Size, Moisture Content, and Soil Gas Permeability Site Average Correlation Scatterplot



	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

Figure 5-12. Element Concentrations and Particle Size Site Average Correlation Scatterplot

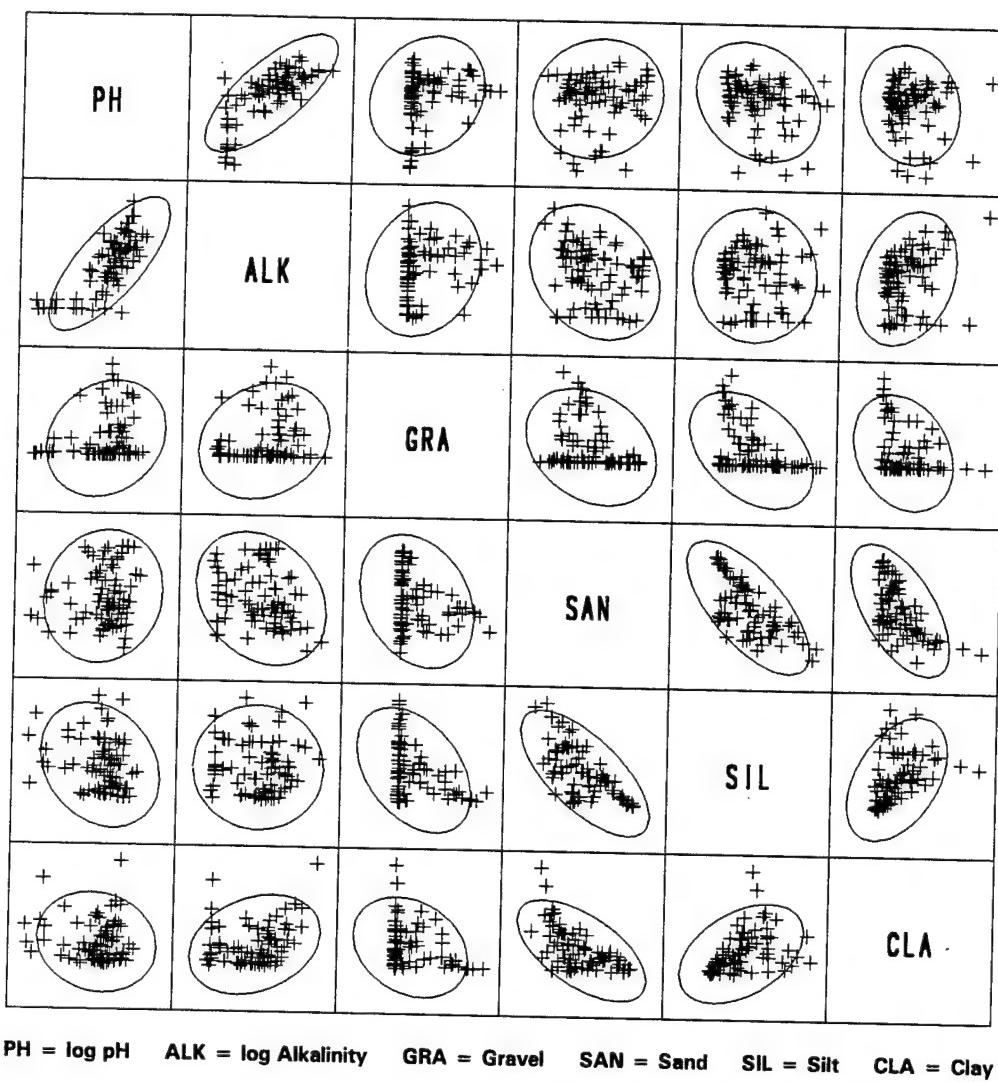


btxsg = log BTEX in Soil Gas tphsg = log TPH in Soil Gas btxs = log BTEX Soil
 tphs = log TPH in Soil GRA = Gravel SAN = Sand SIL = Silt CLA = Clay

	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

Figure 5-13. Contaminant Concentrations and Particle Size Site Average Correlation Scatterplot



PH = log pH ALK = log Alkalinity GRA = Gravel SAN = Sand SIL = Silt CLA = Clay

	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

Figure 5-14. pH, Alkalinity, and Particle Size Site Average Correlation Scatterplot

magnitude of the correlation can be inferred from the shape of the ellipse by comparing it to the key figure. In the key figure, comparable ellipses are displayed for distributions with known correlations of 90%, 60%, 30%, and 0%.

For example, in Figures 5-9 through 5-11, it can be seen that the oxygen utilization rate is most positively correlated with nitrogen (Figure 5-9, correlation coefficient $r=0.40$), moisture (Figure 5-9, $r=0.30$), and soil gas TPH concentrations (Figure 5-10, 0.20), and negatively correlated with sand (Figure 5-11, $r=0.25$) and temperature (Figure 5-10, $r=0.25$). These values indicate that high levels of nitrogen, moisture, and soil gas TPH concentrations and low levels of sand and temperature appear to correlate with high oxygen utilization rates.

It should be noted that the correlation between soil temperature and oxygen utilization rate is of little practical significance in this analysis. At a given site, temperature has been shown to correlate well with microbial activity, which displays peak activity in summer months and low activity in winter months. However, it has been noted that the temperature/microbial activity relationship is very site specific. In other words, microorganisms in Alaska will show peak activity in summer months with comparable oxygen utilization rates to organisms from more temperate climates; however, soil temperatures will be significantly different. Therefore, it is not possible to correlate rates with temperature under such different climatic conditions as were seen at Bioventing Initiative sites.

Among the soil parameters, the correlation coefficient between soil gas BTEX and TPH concentrations is 0.92 (Figure 5-9) and that between pH and alkalinity is 0.75 (Figure 5-9). The correlations between the particle sizes (sand, silt, and clay), moisture, and soil gas permeability are also pronounced.

After taking the log transformation, a second regression model was fitted to the oxygen utilization rate using stepwise regression. Finally, the effect of a cyclic seasonal component on the residuals obtained from the fitted regression model was investigated by including the date that the initial in situ respiration test was conducted.

The final regression model for the oxygen utilization rate is:

$$\begin{aligned} \log(O_2) = & -2.7 + 0.39 \log(NIT) - 0.108(MOI) + \\ & 0.017 \log(TPHsg) * MOI - 0.004 \log(TPHsg) * TMP \end{aligned} \quad (5-4)$$

Each of the effects in the above model is statistically significant at the 0.05 significance level. Note that the effects appearing in the model are consistent with the relationships observed in the bivariate setting. The model explains 41% of the variability in the log-transformed oxygen utilization rate; that is, a 64% correlation between the observed and model-predicted log-transformed oxygen utilization rates. Figure 5-15 illustrates actual versus predicted oxygen utilization rates based on model predictions. As shown, the model appears to explain mid-range oxygen utilization rates fairly well, but low oxygen utilization rates are not predicted as accurately. This may be due to an effect on microbial activity not measured during the Bioventing Initiative, and therefore, unexplained in the model.

5.2.4 Correlation of Oxygen Utilization and Carbon Dioxide Production Rate Ratios With Environmental Parameters

Because in situ biodegradation rates are measured indirectly through measurements of soil gas oxygen and carbon dioxide concentrations, abiotic processes that affect oxygen and carbon dioxide concentration will affect measured biodegradation rates. The factors that may most influence soil gas oxygen and carbon dioxide concentrations are soil pH, soil alkalinity, and iron content.

At nearly all sites included in the Bioventing Initiative, oxygen utilization has proven to be a more useful measure of biodegradation rates than carbon dioxide production. The biodegradation rate in mg of hexane-equivalent/kg of soil per day based on carbon dioxide production usually is less than can be accounted for by the oxygen disappearance. A study conducted at the Tyndall AFB site was an exception. That site had low-alkalinity soils and low-pH quartz sands, and carbon dioxide production actually resulted in a slightly higher estimate of biodegradation (Miller, 1990).

In the case of the higher pH and higher alkalinity soils at sites such as at Fallon NAS and Eielson AFB, little or no gaseous carbon dioxide production was measured (Hinchey et al., 1989; Leeson et al., 1995). This is possibly due to the formation of carbonates from the gaseous evolution of carbon dioxide produced by biodegradation at these sites. A similar phenomenon was encountered

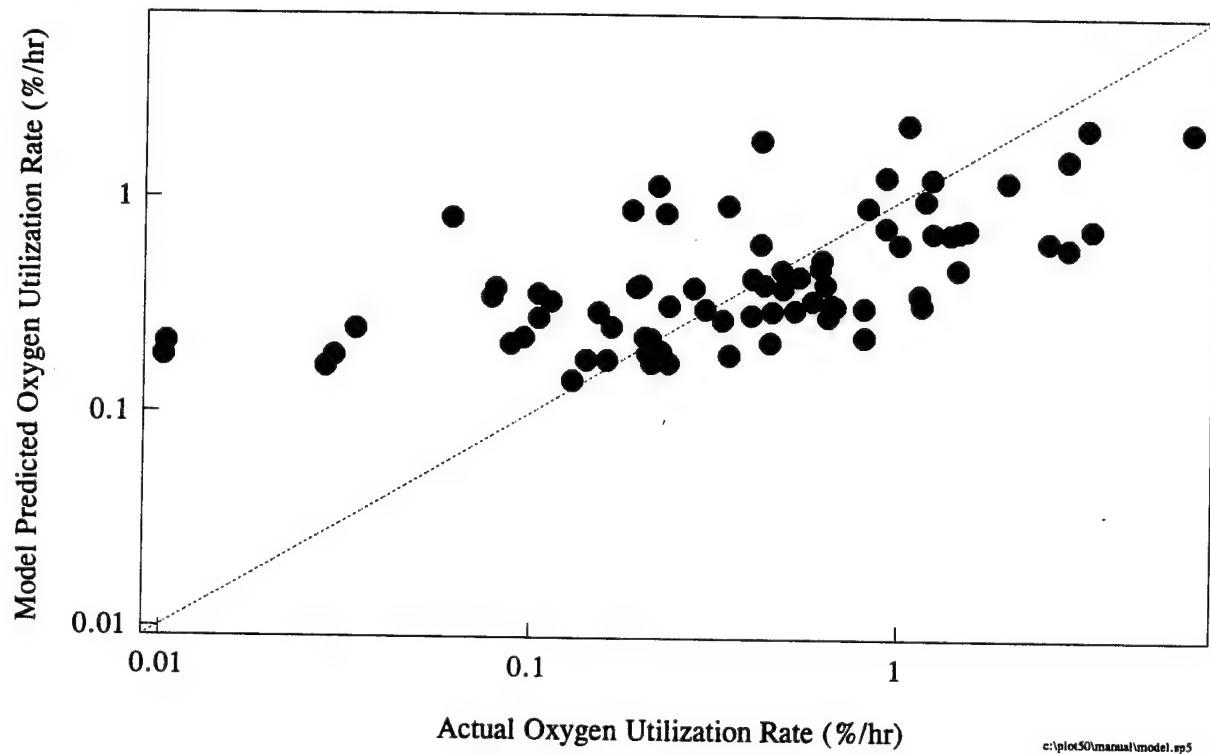


Figure 5-15. Actual Versus Model-Predicted Oxygen Utilization Rates

by van Eyk and Vreeken (1988) in their attempt to use carbon dioxide evolution to quantify biodegradation associated with soil venting.

In order to determine whether pH and alkalinity influenced carbon dioxide production rates at Bioventing Initiative sites, an analysis of the ratio of oxygen utilization to carbon dioxide production versus soil parameters was performed. Due to stoichiometry¹, the ratio of the oxygen utilization to carbon dioxide production rate will not be 1, because for every 9.5 moles of oxygen consumed, 6 moles of carbon dioxide are produced. A square root transformation of the oxygen utilization and carbon dioxide production rate ratio and log transformations of some of the soil parameters were taken whenever the data were not well represented by the normal distribution. Figures 5-9 through 5-11 display the bivariate relationships between the ratio and the soil parameters after the transformation. In these figures, as expected, there is a negative correlation between the ratio and the oxygen utilization rate (Figure 5-9, $r = -0.45$). The correlation of the ratio with clay is the most pronounced (Figure 5-11, $r = -0.40$). The ratio is also negatively correlated with pH (Figure 5-9, $r = -0.25$) and alkalinity (Figure 5-9, $r = -0.30$). As noted previously, pH and alkalinity are strongly positively related (Figure 5-9, $r = 0.75$). The correlations of the ratio with iron, moisture, permeability, and particle sizes are between 0.20 and 0.30 (Figures 5-9 and 5-11).

The statistical methods used to model the ratio of the oxygen utilization rate to carbon dioxide production rate as a function of the soil parameters are similar to those used for the oxygen utilization rate analyses. As a preliminary step, a square root transformation of the ratio and log transformation of some of the soil parameters were taken to obtain more normally distributed data. All the transformations for the soil parameters except clay were consistent with those taken previously to model the oxygen utilization rate. A log transformation of clay was considered as it was more correlated with the ratio.

After applying the transformation, a regression model was fitted to the ratio using forward stepwise regression. The model accounted for the effects of each of the soil parameters (except season) and their interactions. Finally, the effect of a cyclic seasonal component on the residuals obtained from the fitted model was determined by incorporating the date the initial in situ respiration test was conducted.

¹ Refer to Section 3.2.1 for the stoichiometry of hydrocarbon degradation.

The final model for the ratio of the carbon dioxide production rate to the oxygen utilization rate is as follows:

$$\left(\frac{\text{CO}_2 \text{ rate}}{\text{O}_2 \text{ rate}} \right)^{\frac{1}{2}} = 1.28 - 0.38 \log(\text{pH}) - 0.095 \log(\text{clay}) + 0.0007 \log(\text{tphs}) * \text{TMP} \quad (5-5)$$

Each of the effects in the above model is statistically significant at the 0.05 significance level. The model explains 40% of the variability in the transformed ratio. This amounts to 63% correlation between the observed and model-predicted transformed ratios. The effects of pH on the ratio as predicted by the model are presented in Figure 5-16.

The complicated nature of the fitted regression model for the ratio makes the quantification of the effects in the model difficult. However, based on inspection of Figure 5-16, it can be seen that as pH increases, the ratio of the carbon dioxide production rate to the oxygen utilization rate decreases, as would be expected given the formation of carbonates.

5.2.5 Correlation of Soil Gas Permeability With Environmental Parameters

The bivariate relationships between log-transformed soil gas permeability and each of the independent variables of interest are shown in Figure 5-17. In this figure, permeability is most strongly correlated with clay ($r = -0.50$). The magnitudes of the correlations with both moisture and sand are less pronounced and similar.

The statistical methods used here are similar to those described previously for the oxygen utilization rate and the ratio. Forward stepwise regression was used to determine a regression model for the log-transformed soil gas permeability. The independent variables of interest in the modeling were moisture content and the particle sizes (sand, silt, and clay).

The final model describing soil gas permeability is given below:

$$\log(\text{PRM}) = 3.2 - 0.064 \text{ clay} \quad (5-6)$$

Based on this model, clay alone explains 21% of the variability in the log-transformed soil gas permeability. The effect of clay on soil gas permeability as predicted by the model is presented in Figure 5-18. In this figure, the soil gas permeability levels greater than 100 have been censored; that

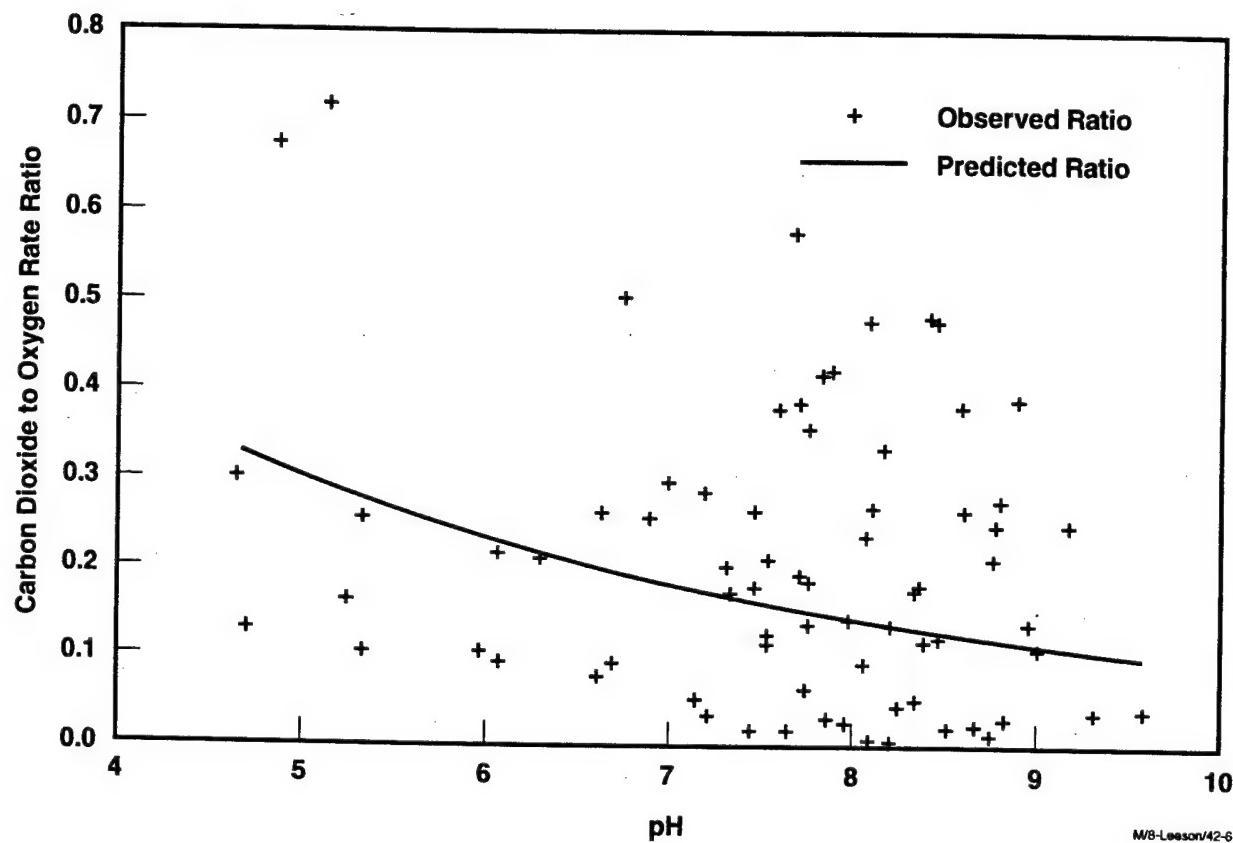
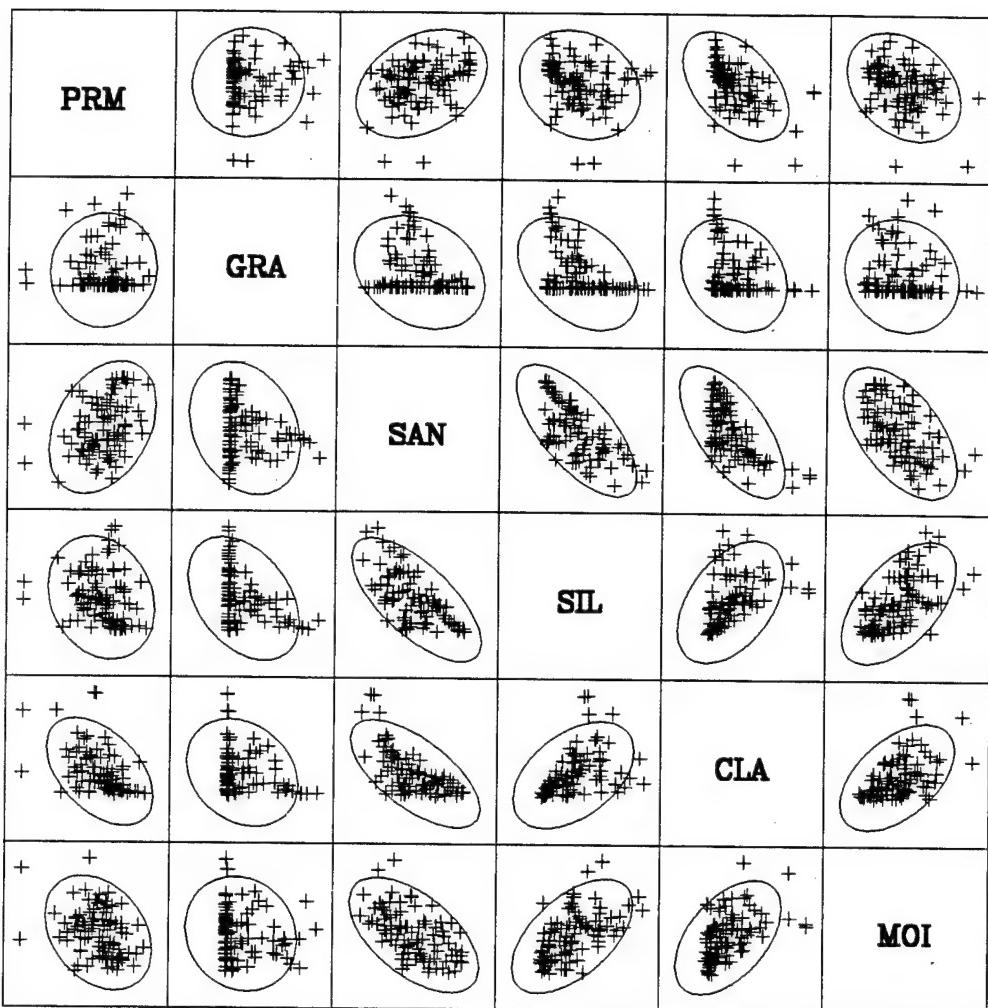


Figure 5-16. Variation of pH and the Effect on Oxygen Utilization to Carbon Dioxide Rate Ratio Based on Model Predictions With Average Levels of Other Parameters



PRM = log Soil Gas Permeability GRA = Gravel SAN = Sand SIL = Silt CLA = Clay MOI = Moisture

	90%	60%	30%	0%
Z1				

Key to Correlation Scatterplots.

Figure 5-17. Soil Gas Permeability, Moisture Content, and Particle Size Site Average Correlation Scatterplot

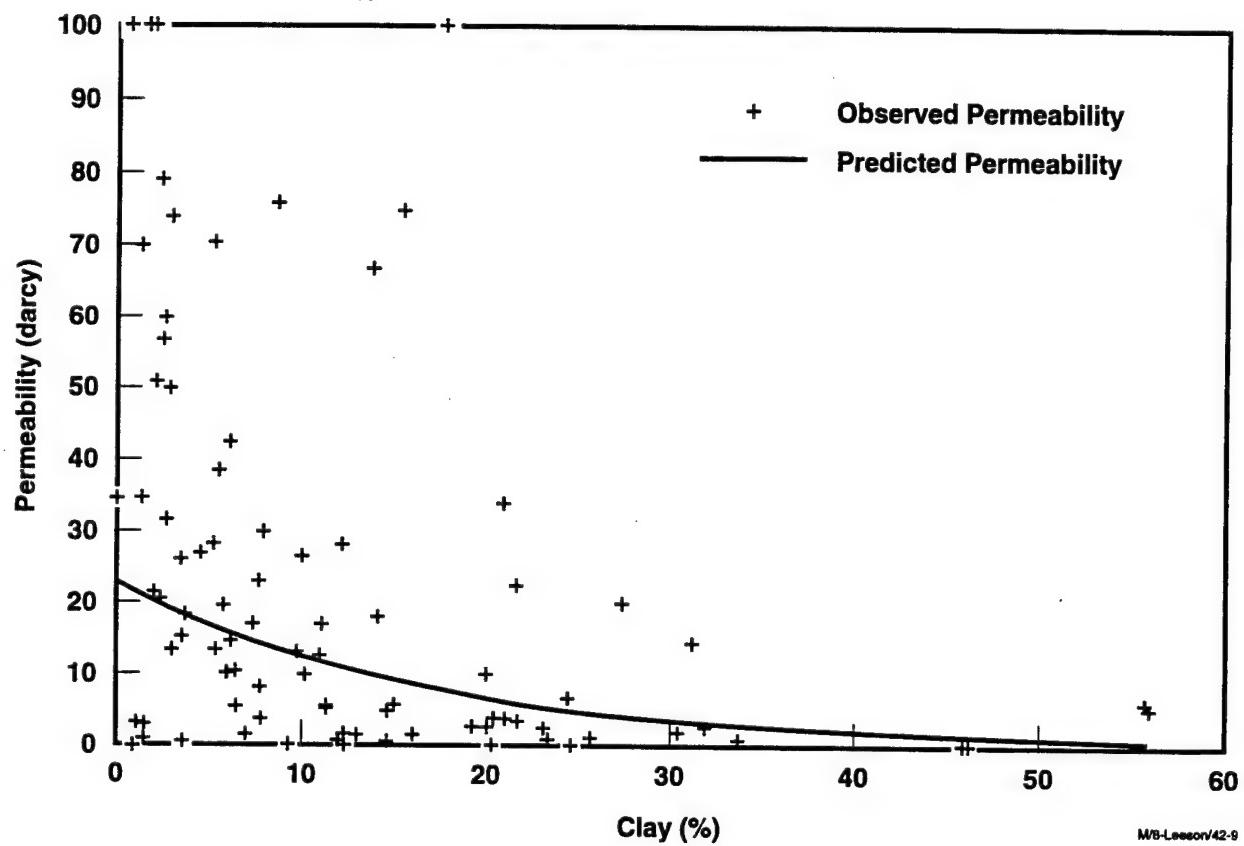


Figure 5-18. Variation of Clay and the Effect on Soil Gas Permeability Based on Model Predictions

is, they were set to a constant value of 100. Based on the regression model it is determined that an increase in clay by 5 units decreases soil gas permeability by 25% on average.

5.2.6 Analyses of Data From Contaminated and Background Areas

As the preliminary step to comparing the data at background and contaminated sites, transformations of the data parameters were considered. These transformations were consistent with those taken previously to address the other objectives of the statistical analysis. After taking the transformation, statistical analyses were performed separately on each parameter (nitrogen, oxygen utilization rate, etc.). The goal of this analysis was to determine significant differences in the levels of each parameter at background and contaminated sites, with particular interest in TKN concentrations. Measurement of TKN accounts for nitrogen sources within cellular material; therefore, it is possible that TKN concentrations may be higher in contaminated areas, where microbial populations may be higher, than in uncontaminated areas. To date, there is no significant difference between TKN concentrations at contaminated sites (average of 232 mg/kg) and those at background areas (average of 226 mg/kg).

5.2.7 Summary

Based on the statistical analyses presented in the previous sections, the following overall conclusions are drawn:

- The relationships between the biodegradation rates and the soil parameters are not very strong. However, some significant relative effects of the soil parameters stand out from the statistical evaluation conducted in the study. Namely, nitrogen, moisture, and soil gas TPH concentrations appear to be the most important characteristics influencing observed field oxygen utilization rates.
- The ratio of the carbon dioxide production rate to the oxygen utilization rate correlates strongly with pH and clay levels in the soil.
- Soil gas permeability correlates with each of the particle sizes (sand, silt, and clay) and moisture content; however, the relative effect of clay on permeability is most important.

The Bioventing Initiative has provided a large database of information useful in the design and implementation of bioventing systems. The statistical analyses provide guidelines for determining which parameters are most important to bioventing technology. However, these data must be balanced by experience and site-specific data. For example, sites with relatively low soil nitrogen concentrations should not be discarded as bioventing sites for this reason alone, nor should it be assumed that nitrogen addition at such sites will increase oxygen utilization rates. Data collected from the U.S. Air Force Bioventing Initiative have shown that even sites with low soil nutrient concentrations can exhibit significant microbial activity and would therefore respond well to bioventing.

6.0 REFERENCES

- Aggarwal, P.K., J.L. Means, and R.E. Hinchee. 1991. "Formulation of Nutrient Solutions for In Situ Bioremediation." In: R.E. Hinchee and R.F. Olfenbuttel (Eds.), *In Situ Bioreclamation*, Butterworth-Heinemann, Stoneham, MA. pp. 51-66.
- Alleman, B.C., R.E. Hinchee, R.C. Brenner, and P.T. McCauley. 1995. "Bioventing PAH Contamination at the Reilly Tar Site," In: R.E. Hinchee, R. N. Miller, and P.C. Johnson (Eds.), *In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes*, Battelle Press, Columbus, OH. pp. 473-482.
- American Petroleum Institute. 1987. *Field Study of Enhanced Subsurface Biodegradation of Hydrocarbons Using Hydrogen Peroxide as an Oxygen Source*. API Publication #4448, Washington, D.C., 1987.
- Anonymous. 1986. "In Situ Reclamation of Petroleum Contaminated Sub-Soil by Subsurface Venting and Enhanced Biodegradation." *Research Disclosure*, No. 26233, 92-93.
- Atlas, R.M. 1986. "Microbial Degradation of Petroleum Hydrocarbons: An Environmental Perspective." *Microbiol. Rev.*, 45:180-209.
- Baker, J.N., D.A. Nickerson, and P.R. Guest. 1993. "Use of a Horizontal Air-Dispersion System to Enhance Biodegradation of Diesel Fuel Contaminated Sites." In: *Proceedings of the 1993 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*. Presented by The American Petroleum Institute and The Association of Ground Water Scientists and Engineers. Water Well Journal Publishing Company, Dublin, OH.
- Battelle. 1994. "Bioremediation of Hazardous Wastes at CERCLA and RCRA Sites: Hill AFB 280 Site, Low-Intensity Bioreclamation", Report Prepared by Battelle Memorial Institute for the U.S. Environmental Protection Agency, January, 1994.
- Bennedsen, M.B., J.P. Scott, and J.D. Hartley. 1987. "Use of Vapor Extraction Systems for In Situ Removal of Volatile Organic Compounds from Soil." In: *Proceedings of National Conference on Hazardous Wastes and Hazardous Materials*, Washington, DC. pp. 92-95.
- Bilbo, C.M., E. Arvin, and H. Holst. 1992. "Modelling the Growth of Methane-Oxidizing Bacteria in a Fixed Biofilm." *Water Research*, 26:301-309.
- Britton, L.N.. 1985. *Field Studies on the Use of Hydrogen Peroxide to Enhance Microbial Degradation of Gasoline*. API Publication #4389, Washington, D.C., 1985.
- Brock, T.D., D.W. Smith, and M.T. Madigan. 1984. Biology of Microorganisms, 4th Edition, Prentice-Hall, Inc., Englewood Cliffs, NJ.
- Brown, R.A. and J.R. Crosbie. 1994. "Oxygen Sources for In Situ Bioremediation." *Bioremediation: Field Experience*. Lewis Publishers, Boca Raton, FL, pp. 311-331.

Brown, R.A., R.D. Norris, and R.L. Raymond. 1984. "Oxygen Transport in Contaminated Aquifers," in *Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, National Water Well Association, Columbus, OH, November 1984.

Conner, A.T. 1989. "Case Study on Soil Venting." *Pollution Engineering*, 20(8):74-78.

DeVinny, J.S., L.G. Everett, J.C.S. Lu, and R.L. Stollar. 1990. Subsurface Migration of Hazardous Wastes. Van Nostrand Reinhold.

Downey, D.C. and J.F. Hall. 1994. Addendum One to Test Plan and Technical Protocol for a Field Treatability Test for Bioventing - Using Soil Gas Surveys to Determine Bioventing Feasibility and Natural Attenuation Potential, U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, TX.

Downey, D.C., J.F. Hall, R.N. Miller, A. Leeson, and R.E. Hinchee. 1994. Bioventing Performance and Cost Summary, February, 1994, U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, TX.

Downey, D.C., R.E. Hinchee, M.S. Westray, and J.K. Slaughter. 1988. "Combined Biological and Physical Treatment of a Jet Fuel-Contaminated Aquifer," in *Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*, National Water Well Association, Columbus, OH, November 1988, pp.627-645.

Dragun, J. 1988. "Microbial Degradation of Petroleum Products in Soil." In E.J. Calabrese and P.T. Kostecki (Eds.), *Soils Contaminated by Petroleum: Environmental and Public Health Effects*. John Wiley & Sons, Inc., New York, NY. pp. 289-300.

Dupont, R.R., W.J. Doucette, and R.E. Hinchee. 1991. "Assessment of *In Situ* Bioremediation Potential and the Application of Bioventing at a Fuel-Contaminated Site." In R.E. Hinchee and R.F. Olfenbuttel (Eds.), *In Situ Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation*, pp. 262-282. Butterworth-Heinemann, Stoneham, MA.

Ely, D.L., and D.A. Heffner. 1988. "Process for In-Situ Biodegradation of Hydrocarbon Contaminated Soil." U.S. Patent Number 4,765,902.

Engineering-Science. 1992. *Interim Pilot Test Results Report for Installation Restoration Program Site 3, Fire Training Area, Battle Creek ANGB, Michigan*, Report prepared for the U.S. Air Force Center for Environmental Excellence, Brooks AFB, Texas.

Foor, D.C. and R.E. Hinchee. 1993. *Long-Term Bioventing System Installation at Tank #7 and Tank #5 of the Alyeska Valdez Marine Terminal, Valdez, Alaska*, Report prepared for America North/EMCON, Anchorage, Alaska, November 1993.

Hinchee, R.E., and M. Arthur. 1991. "Bench-Scale Studies of the Soil Aeration Process for Bioremediation of Petroleum Hydrocarbons." *J. Appl. Biochem. Biotech.*, 28/29:901-906.

Hinchee, R.E., and S.K. Ong. 1992. "A Rapid In Situ Respiration Test for Measuring Aerobic Biodegradation Rates of Hydrocarbons in Soil." *Journal of the Air & Waste Management Association*, 42(10):1305-1312.

Hinchee, R.E., D.C. Downey, and T. Beard. 1989. "Enhancing Biodegradation of Petroleum Hydrocarbons Fuels in the Vadose Zone Through Soil Venting", In: *Proceedings of the 1993 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration* presented by The American Petroleum Institute and The Association of Ground Water Scientists and Engineers. Water Well Journal Publishing Company, Dublin, OH, pp. 235-248.

Hinchee, R.E., S.K. Ong, R.N. Miller, D.C. Downey, and R. Frandt. 1992. *Test Plan and Technical Protocol for a Field Treatability Test for Bioventing*, Rev. 2. U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, TX.

Hinchee, R.E. and G. Smith. 1991. Unpublished Data, Battelle, Columbus, Ohio.

Hinchee, R.E., D.C. Downey, and P. Aggarwal. 1991a. "Use of Hydrogen Peroxide as an Oxygen Source for In Situ Biodegradation: Part I. Field Studies." *J. Hazardous Materials*, 27:287-299.

Hinchee, R.E., D.C. Downey, R.R. Dupont, P. Aggarwal, and R.N. Miller. 1991b. "Enhancing Biodegradation of Petroleum Hydrocarbon through Soil Venting." *J. Hazardous Materials*, 27:315-325.

Hinchee, R.E., D.C. Downey, J.K. Slaughter, D.A. Selby, M. Westray, and G.M. Long. 1989. HQ AFESC/RDVW ESK-TR-88-78. *Enhanced Bioreclamation of Jet Fuels: A Full-Scale Test at Eglin Air Force Base, Florida*. ESL/TR/88-78. Air Force Engineering and Services Center.

Hopkins, G.D., J. Munakata, L. Semprini, and P.L. McCarty. 1993. "Trichloroethylene Concentration Effects on Pilot Field-Scale In-Situ Groundwater Bioremediation by Phenol-Oxidizing Microorganisms." *Environ. Sci. Technol.*, 27(12):2542-2547.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Meylan, and E.m. Michalenko. 1991. Handbook of Environmental Degradation Rates. Lewis Publishers, Chelsea, MI.

Huling, S.G., B.E. Bledsoe, and M.V. White. 1990. *Enhanced Biodegradation Utilizing Hydrogen Peroxide as a Supplemental Source of Oxygen: A Laboratory and Field Study*. EPA/600-290-006. 48 pp.

Johnson, P.C., M.W. Kembowski, and J.D. Colthart. 1990. "Quantitative Analysis for the Cleanup of Hydrocarbon-Contaminated Soils by In-Situ Soil Venting." *Ground Water*, 28(3). May-June.

Kittel, J.A., R.E. Hinchee, and M. Raj. 1995. *Full-Scale Startup of a Soil Venting-Based In Situ Bioremediation Field Pilot Study at Fallon NAS, Nevada*, Report Prepared for the Naval Facilities Engineering Services, Port Hueneme, CA, February, 1994.

Leeson, A. and R.E. Hinchee. 1994. *Field Treatability Study at the Greenwood Chemical Superfund Site, Albemarle County, Virginia*, Report Prepared for the U.S. Environmental Protection Agency, Cincinnati, OH, January, 1994.

Leeson, A., R.E. Hinchee, J.A. Kittel, E.A. Foote, G. Headington, and A. Pollack. 1995. *Bioventing Feasibility Study at the Eielson AFB Site*, Report Prepared for the Environics Directorate of the Armstrong Laboratory, Tyndall AFB, FL, September, 1995.

Lund, N.-Ch., J. Swiniarski, G. Gudehus, and D. Maier. 1991. "Laboratory and Field Tests for a Biological *In Situ* Remediation of a Coke Oven Plant." In R.E. Hinchee and R.F. Olfenbuttel (Eds.), *In Situ Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation*. Butterworth-Heinemann Publishing Company, Stoneham, MA. pp. 396-412.

Lyman, W.J., P.J. Reidy, and B. Levy. 1992. Mobility and Degradation of Organic Contaminants in Subsurface Environments, C.K. Smoley, Inc., Chelsea, MI.

Metcalf and Eddy. 1979. *Wastewater Engineering Treatment, Disposal, Reuse*. McGraw-Hill, New York, NY. 920 pp.

Miller, R.N. 1990. "A Field Scale Investigation of Enhanced Petroleum Hydrocarbon Biodegradation in the Vadose Zone Combining Soil Venting as an Oxygen Source with Moisture and Nutrient Additions." Ph.D. Dissertation. Utah State University, Logan, UT.

Miller, R.N., C.C. Vogel, and R.E. Hinchee. 1991. "A Field-Scale Investigation of Petroleum Hydrocarbon Biodegradation in the Vadose Zone Enhanced by Soil Venting at Tyndall AFB, Florida." In R.E. Hinchee and R.F. Olfenbuttel (Eds.), *In Situ Bioreclamation*. Butterworth-Heinemann, Stoneham, MA. pp. 283-302.

Miller, R.N., D.C. Downey, V.A. Carmen, R.E. Hinchee, and A. Leeson. 1993. "A Summary of Bioventing Performance at Multiple Air Force Sites." In *Proceedings of the 1993 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*. November 10 - 12, Houston, TX.

Morgan, P. and R.J. Watkinson. 1992. "Factors Limiting the Supply and Efficiency of Nutrient and Oxygen Supplements for the *In Situ* Biotreatment of Contaminated Soil and Groundwater," *Water Research*, 26(1):73-78.

Mormile, M.R., S. Liu, and J.M. Suflita. 1994. "Anaerobic Biodegradation of Gasoline Oxygenates: Extrapolation of Information to Multiple Sites and Redox Conditions," *Environmental Science & Technology*, 28(9):1727-1732.

Newman, B., M. Martinson, G. Smith, and L. McCain. 1993. "Enhanced Biodegradation of Hydrocarbons *In-Situ* via Bioventing." In: *Proceedings of the 1993 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration*. Presented by the American Petroleum Institute and the Association of Ground Water Scientists and Engineers. Water Well Journal Publishing Company, Dublin, OH.

Oak Ridge National Laboratory. 1989. Soil Characteristics: Data Summary, Hill Air Force Base Building 914 Fuel Spill Soil Venting Project. An unpublished report to the U.S. Air Force.

Ong, S.K., A. Leeson, R.E. Hinchee, J. Kittel, C.M. Vogel, G.D. Sayles, and R.N. Miller. 1994. "Cold Climate Application of Bioventing," In R.E. Hinchee, B.C. Alleman, R.E. Hoeppel, and R.N. Miller (Eds.), *Hydrocarbon Bioremediation*. Lewis Publishers, Boca Raton, FL, pp. 444-453.

Ostendorf, D.W. and D.H. Kampbell. 1989. "Vertical Profiles and Near Surface Traps for Field Measurement of Volatile Pollution in the Subsurface Environment." In: *Proceedings of NWWA Conference on New Techniques for Quantifying the Physical and Chemical Properties of Heterogeneous Aquifers*, Dallas, TX. Westarp Wiss., Essen, Germany, pp. 475-485.

Phelps, M.B., F.T. Stanin, and D.C. Downey. 1995. In: R.E. Hinchee, R. N. Miller, and P.C. Johnson (Eds.), *In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes*, Battelle Press, Columbus, OH. pp. 277-282.

Sayles, G.D., R.C. Brenner, R.E. Hinchee, A. Leeson, C.M. Vogel, and R.N. Miller. 1994a. "Bioventing of Jet Fuel Spills I: Bioventing in a Cold Climate with Soil Warming at Eielson AFB, Alaska," *Symposium on Bioremediation of Hazardous Wastes: Research, Development and Field Applications*. EPA/600/R-94/075, June 1994, pp. 15-21.

Sayles, G.D., R.C. Brenner, R.E. Hinchee, and E. Elliott. 1994b. "Bioventing of Jet Fuel Spills II: Bioventing in a Deep Vadose Zone at Hill AFB, Utah." In *Symposium on Bioremediation of Hazardous Wastes: Research, Development and Field Applications*. EPA/600/R-94/075, June 1994, pp. 22-28.

Schumb, W.C., C.N. Satterfield and R.L. WEntworth. 1955. Hydrogen Peroxide, Van Nostrand Reinhold, New York, NY.

Spain, J.C., J.D. Milligan, D.C. Downey and J.K. Slaughter. 1989. "Excessive Bacterial Decomposition of H₂O₂ During Enhanced Biodegradation", *J. Groundwater*, 27:163-167.

Staatsuitgeverij. 1986. Proceedings of a Workshop, 20-21 March, 1986. *Bodembeschermingsreeks* No. 9; *Biotechnologische Bodemsanering*, pp. 31-33. Rapportnr. 851105002, ISBN 90-12-054133, Ordernr. 250-154-59; Staatsuitgeverij Den Haag: The Netherlands.

Texas Research Institute. 1980. *Laboratory Scale Gasoline Spill and Venting Experiment*. American Petroleum Institute, Interim Report No. 7743-5:JST.

Texas Research Institute. 1984. *Forced Venting to Remove Gasoline Vapor from a Large-Scale Model Aquifer*. American Petroleum Institute, Final Report No. 82101-F:TAV.

Urlings, L.G.C.M., H.B.R.J. van Vree, and W. van der Galien. 1990. "Application of Biotechnology in Soil Remediation." *Envirotech Vienna*. pp. 238-251.

U.S. Environmental Protection Agency. 1993. "Engineering Issue — In Situ Bioremediation of Contaminated Unsaturated Subsurface Soils." Draft. EPA/540/S-93/501. Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, Ada, OK; and Office of Solid Waste and Emergency Response, Washington, DC.

van Eyk, J. and C. Vreeken. 1988. "Venting-Mediated Removal of Petrol from Subsurface Soil Strata as a Result of Stimulated Evaporation and Enhanced Biodegradation." *Med. Fac. Landbouww. Rijksuniv. Gent*, 53(4b):1873-1884.

van Eyk, J. and C. Vreeken. 1989a. "Model of Petroleum Mineralization Response to Soil Aeration to Aid in Site-Specific, In Situ Biological Remediation." In: Jousma et al. (Eds.), *Groundwater Contamination: Use of Models in Decision-Making, Proceedings of an International Conference on Groundwater Contamination*. Kluwer, Boston/London. pp. 365-371.

van Eyk, J. and C. Vreeken. 1989b. "Venting-Mediated Removal of Diesel Oil from Subsurface Soil Strata as a Result of Stimulated Evaporation and Enhanced Biodegradation." In: *Hazardous Waste and Contaminated Sites, Envirotech Vienna*, Vol. 2, Session 3. ISBN 389432-009-5. Westarp Wiss., Essen, Germany. pp. 475-485.

van Eyk, J. 1994. "Venting and Bioventing for the In Situ Removal of Petroleum From Soil", In R.E. Hinchee, B.C. Alleman, R.E. Hoeppel, and R.N. Miller (Eds.), *Hydrocarbon Bioremediation*. Lewis Publishers, Boca Raton, FL, pp. 243-251.

Wackett, L.P. and D.T. Gibson. 1992. "Degradation of Trichloroethylene by Toluene Dioxygenase in Whole-Cell Studies with *Pseudomonas putida* F1", *Applied and Environmental Microbiology*, 54(7):1703-1708.

Ward, C.H. 1988. "A Quantitative Demonstration of the Raymond Process for In-Situ Bioremediation of Contaminated Aquifers." *Proceedings of NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater*. pp. 723-746.

Wiedemeier, T.H., J.T. Wilson, D.H. Campbell, R.N. Miller, and J.E. Hansen. 1995. *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Ground Water*, Report Prepared for the U.S. Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, Texas, April 1995.

Wilson, J.T. and C.H. Ward. 1986. "Opportunities for Bioremediation of Aquifers Contaminated with Petroleum Hydrocarbons." *J. Ind. Microbiol.*, 27: 109-116.

Zachary, S.P. and L.G. Everett. 1993. "In-Situ Active/Passive Bioreclamation of Vadose Zone Soils Contaminated with Gasoline and Waste Oil Using Soil Vapor Extraction/Bioventing: Laboratory Pilot Study to Full Scale Site Operation." In: *Proceedings of the 1993 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration* presented by The American Petroleum Institute and The Association of Ground Water Scientists and Engineers. Water Well Journal Publishing Company, Dublin, OH.

APPENDIX A

GLOSSARY

GLOSSARY

abiotic - not relating to living things, not alive

acidity - measure of the hydrogen ion concentration of a solution

adsorption - the process by which molecules collect on and adhere to the surface of an adsorbent solid due to chemical and/or physical forces

aeration - process of supplying or introducing air into a medium such as soil or water

aerobic - living, active, or occurring only in the presence of oxygen

air sparging - general term for the technology of introducing gases, usually air, beneath the water table to promote site remediation. Air sparging can be divided into two distinct processes: in-well aeration and air injection

alkalinity - measure of the hydroxide ion concentration of a solution

alluvial - relating to flowing water as in a stream or river

anaerobic - living, active, or occurring only in the absence of oxygen

aquifer - a water-bearing layer of permeable rock, sand, or gravel

bentonite - clay composed of volcanic ash decomposition which is used to seal wells (hole plug)

bioavailability - a general term to describe the accessibility of contaminants to the degrading populations. Bioavailability consists of: (1) a physical aspect related to phase distribution and mass transfer, and (2) a physiological aspect related to the suitability of the contaminant as a substrate

biodegradable - a material or compound which is able to be broken down by natural processes of living things such as metabolism by microorganisms

biodegradation - the act of breaking down material (usually into more innocuous forms) by natural processes of living things such as metabolism by microorganisms

biodegradation rate - the mass of contaminant metabolized by microorganisms per unit time. In soil contamination this is normalized to the mass of soil and is usually expressed as *mg contaminant degraded/kg soil-day* (mg/kg-day).

biofilm - a structure in which bacteria fixed to a surface produce a protective extracellular polysaccharide layer

biofiltration - process using microorganisms immobilized as a biofilm on a porous filter substrate such as peat or compost to separate contaminants. As the air and vapor contaminants pass through the filter, contaminants transfer from the gas phase to the biolayer where they are metabolized

biomass - the amount of living matter (in a specified area)

bioreactor - a container or area in which a biological reaction or biological activity takes place

bioreclamation - the process of making a contaminated site usable again through biological processes

bioremediation - general term for the technology of using biological processes such as microbial metabolism to degrade soil and water contaminants and decontaminate sites

bioslurping - a technology application that teams vacuum-assisted free-product recovery with bioventing to simultaneously recover free product and remediate the vadose zone

bioventing - the process of aerating subsurface soils by means of installed vents to stimulate in situ biological activity and optimize bioremediation with some volatilization occurring

blower - equipment which produces a constant stream of forced air. Blowers are sized in terms of horsepower

capillarity - the action by which a liquid is held to a solid by surface tension

capillary fringe - the first layer of rock above a layer in which water is held by capillarity

catalyst - a substance which initiates a chemical reaction allows a reaction to proceed under different conditions than otherwise possible, or accelerates a chemical reaction; catalysts are not consumed in the reaction; enzymes are catalysts.

catalytic oxidation - an incineration process which uses catalysts to increase the oxidation rate of organic contaminants allowing equivalent destruction efficiency at a lower temperature than flame incineration

clay - fine-grained soil that can exhibit putty-like properties within a range of water content and is very strong when air-dry

co-metabolic process - metabolism of a less favored substrate occurring during the metabolism of the primary substrate

cone of depression - area of lowered water table around a well site due to active pumping

contaminant - something that makes material in contact with it impure, unfit, or unsafe; a pollutant

diffusion - process of passive transport through a medium motivated by a concentration gradient

diffusivity - diffusion coefficient; the amount of material, in grams, which diffuses across an area of 1 square centimeter in 1 second due to a unit concentration gradient, (particular to compound and medium pair)

electron acceptor - relatively oxidized compounds which take electrons from electron donors during cellular respiration resulting in the release of energy to the cell

electron donor - organic carbon, or reduced inorganic compounds, which give electrons to electron acceptors during cellular respiration resulting in the release of energy to the cell

enzyme - biologically produced, protein-based catalyst

ex situ - refers to a technology or process for which contaminated material must be removed from the site of contamination for treatment

facultative - a microbial trait enabling aerobic or anaerobic respiration, depending on environment

first order reaction - a chemical reaction in which an increase (or decrease) in reactant concentration results in a proportional increase (or decrease) in the rate of the reaction

head - the pressure difference between two places, an energy term expressed in length units

immiscible - refers to liquids which do not form a single phase when mixed; e.g. oil and water

in situ - refers to a technology or treatment process which can be carried out within the site of contamination

in situ respiration test - test used to provide rapid field measurement of in situ biodegradation rates to determine the potential applicability of bioventing at a contaminated site and to provide information for a full-scale bioventing system design

in-well aeration - the process of injecting gas into a well to produce an in-well airlift pump effect

mineralization - the complete conversion of an organic compound to inorganic products (principally water and carbon dioxide)

miscible - refers to liquids which form a single phase when mixed; e.g. ethanol and water

nitrogen fixation - the metabolic assimilation of atmospheric nitrogen by soil microorganisms and its release for plant use upon the death of the microorganisms

nutrients - constituents required to support life and growth

off-gas - gas which leaves a site, typically from a point source during extraction operations

oxidation - chemical process which results in a net loss of electrons in an element or compound

oxygen utilization rate - rate of reduction of the in situ oxygen content of soil gas due to biological and chemical action

ozonation - the injection of ozone into a contaminated site

packed bed thermal treatment - process which oxidizes organic contaminants by passing the off-gas stream through a heated bed of ceramic beads resulting in the destruction of the organic compounds

perched aquifer - unconfined groundwater separated from an underlying main body of groundwater by a low-permeability rock layer which blocks the vertical movement of water

permeability - measure of the ability of liquid or gas to move through pores and openings in a material

pH - measure of the alkalinity or acidity of a solution, the negative log of the hydrogen ion concentration

photocatalytic oxidation - process by which volatile organic compounds are converted to carbon dioxide and water by exposure to ultraviolet (UV) light

pore space - the open space in a material through which liquid and gas can move

porosity - measure of the amount of available space in a material through which liquid and gas can move

primary substrate - substrate which provides the majority of the growth and energy requirements for cells

pump and treat technology - treatment method in which the contaminated water is pumped out of the contaminated site and then treated off site before being returned

radius of influence - the maximum distance from the air extraction or injection well where vacuum or pressure (soil gas movement) occurs

radius of oxygen influence - the radius to which oxygen has to be supplied to sustain maximal biodegradation; a function of both air flowrates and oxygen utilization rates, and therefore depends on site geology, well design, and microbial activity

Raoult's law - physical chemical law which states that the vapor pressure of a solution is equal to the mole fraction of the solvent multiplied by the vapor pressure of the pure solvent

reduction - chemical process which results in a net gain of electrons to an element or compound

remediation - activity involved with reducing the hazard from a contaminated site

respiration rate - see oxygen utilization rate

sand - unconsolidated rock and mineral particles with diameters ranging from 1/16- to 2 mm

saturated zone - the layers of soil which lie below the groundwater table

silt - unconsolidated rock and mineral particles with diameters ranging from 0.0002-0.05 mm

soil vacuum extraction (SVE) - a process designed and operated to maximize the volatilization of low-molecular-weight compounds, with some biodegradation occurring soil gas permeability - a soil's capacity for fluid flow, varies according to grain size, soil uniformity, porosity, and moisture content

sorb - to take up or hold by means of adsorption or absorption

substrate - the base on which an organism lives; reactant in microbial respiration reaction (electron donor, nutrient)

surfactant - substance which lowers the surface tension of a liquid

treatability - ability of a site to be remediated

vacuum-enhanced pumping - use of a vacuum pump to lift groundwater, or other liquids or gases, from a well while producing a reduced pressure in the well

vadose zone - the zone of soil below the surface and above the permanent water table

vent well - a well designed to facilitate injection or extraction of air to/from a contaminated soil area

volatile - easily vaporized at relatively low temperatures

volatilization - process of vaporizing a liquid into a gas

zero order reaction - a chemical reaction in which an increase (or decrease) in reactant concentration results in no change in the rate of reaction (as long as some reactant is present)

APPENDIX B
DATA FROM BIOVENTING INITIATIVE SITES

TABLE OF CONTENTS

Table B-1.	Bioventing Initiative Results: Soil Chemical Characterization	B-2
Table B-2.	Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations	B-8
Table B-3.	Bioventing Initiative Results: Average BTEX and TPH Soil Gas Concentrations	B-17
Table B-4.	In Situ Respiration Test Results at Bioventing Initiative Sites	B-27

Table B-1. Bioventing Initiative Results: Soil Chemical Characterization

Air Force Base	Site	pH	Alkalinity (mg/kg)	TKN (mg/kg)	Total Phosphorus (mg/kg)	Iron Content (mg/kg)
AFP 4	FSA-1	8.8	210	33	270	7,450
	FSA-3	7.7	365	190	340	9,800
AFP PJKS	ST-35	7.5	NS	490	46	NS
	Battle Creek Fire Training Area	8.2	170	73	165	5,050
Beale	Site 3	7.7	87	105	400	27,500
	Site 18	7.4	67	42	250	26,400
Bolling	Site 11	8.2	240	15	820	17,500
	Building 18	4.9	<50	48	85	15,300
Camp Pendleton	Former Storage Tank Farm	8.1	910	100	170	9,610
	Site 1	7.7	120	73	46	3,360
Cannon	SWMU 70	8.4	1,150	190	76	6,570
	FTA-2	7.7	165	18	280	860
Cape Canaveral	Facility 1748	8.5	400	110	310	900
	Facility 44625D	9.2	265	74	190	1,380
Charleston	Facility 44625E	8.8	350	54	270	970
	FT-03	7.1	280	350	350	2,940
Davis Monthan	Site ST-27	6.7	130	62	75	8,400
	Site SS-41	4.7	<50	61	37	530
Dover	Site 35	8.3	360	32	760	15,700
	Site 36	8.1	220	57	450	12,700
Dover	ST-04	5.3	36	48	270	4,700

Table B-1. Bioventing Initiative Results: Soil Chemical Characterization (Continued)

Air Force Base	Site	pH	Alkalinity (mg/kg)	TKN (mg/kg)	Total Phosphorus (mg/kg)	Iron Content (mg/kg)
Dover (continued)	North Storage Tank Farm	5.5	<50	410	100	8,740
	Site FT40	8.7	3,130	180	200	16,900
Dyess	Site FT41	8.8	2,790	240	280	19,500
	Site 21	9.3	730	26	650	9,960
Edwards	Site 16	9.6	640	22	630	12,500
	Site 43	8.9	500	150	360	13,400
Eglin	FTA Hurleburt Field	8.2	300	74	33	670
	Old Eglin FTA	7.5	170	<43	24	1,600
Eielson	ST-10	6.3	<50	390	7.4	10,400
	Site 48-E2	7.8	240	320	650	17,400
Ellsworth	Site 48-E3	7.5	230	690	790	16,700
	Area D Bulk Fuel Storage	8.5	1,150	320	500	15,000
Ehmendorf	Bldg 102 Base Fuel Station	8.6	640	24	1,000	36,800
	43/45 Valve Pit	7.2	100	64	3.5	24,800
FE Warren	ST-61	7.7	160	78	1,200	23,700
	ST-71	7.8	200	110	3.1	28,000
Galena	43/55 Pumphouse	7.5	87	66	1,200	25,300
	Fire Training Pit	7.8	1,300	1,300	440	20,200
Galena	Spill Site	8.2	340	55	320	11,200
	Saddle Tank Farm	7.5	520	800	730	21,400
Power Plant	Power Plant	7.8	490	620	710	24,200

Table B-1. Bioventing Initiative Results: Soil Chemical Characterization (Continued)

Air Force Base	Site	pH	Alkalinity (mg/kg)	TKN (mg/kg)	Total Phosphorus (mg/kg)	Iron Content (mg/kg)
Galena (continued)	Million Gallon Hill	NS	NS	NS	NS	NS
	Campion POL Leak Site	8.1	300	710	570	15,200
Hanscom	Building 1639	6.0	<50	630	320	7,620
	Building 1812	6.6	58	60	530	6,810
Hickam	Area H	9.0	1,500	30	3,400	75,100
	Area K	8.3	860	1,700	2,300	34,100
Hill	Site 2 FSA	4.7	35	38	470	99,000
	Site 204.1	7.8	740	140	NS	5,270
Keesler	Site 214.1	NS	NS	NS	NS	NS
	Site 228	NS	NS	NS	NS	NS
Kelly	Site 924	8.0	74	120	710	6,500
	Site 1705	NS	NS	NS	NS	NS
Johnston Island	Site 388	6.8	52	350	NS	9,380
	Site 40002	NS	NS	NS	390	NS
Keesler	Site 510.8	8.7	340	100	2,200	4,700
	Old Fire Training Area	8.9	540	440	370	270
Keesler	Former POL Tank Farm	9.0	405	185	520	115
	Storage Tanks 260 and 261	9.0	355	140	340	84
Kelly	SWMU 66	7.5	260	102	190	4,300
	AOC A	7.0	250	43	35	2,100
Kelly	Site S-4	7.5	500	690	620	16,000

Table B-1. Bioventing Initiative Results: Soil Chemical Characterization (Continued)

Air Force Base	Site	pH	Alkalinity (mg/kg)	TKN (mg/kg)	Total Phosphorus (mg/kg)	Iron Content (mg/kg)
Kelly (continued)	Site FC-2	8.2	750	590	790	13,400
	Site B-2093	8.2	1,100	310	880	14,000
	Site D-10	7.7	1,100	640	310	13,300
Kirtland	Fire Training Area 13	8.4	340	58	300	11,200
	Fire Training Area 14	7.0	380	200	1,000	26,200
	POL Area	7.9	98	22	140	2,190
KI Sawyer	Tank 191	7.0	260	590	930	24,900
	Fire Training Site 1	6.1	86	710	130	53,000
	Spill Site 18	6.1	<50	390	140	36,300
Little Rock	Building 125	8.7	440	87	1,200	8,900
	Building 241	7.5	830	120	1,600	33,800
	Gate 3	8.4	310	65	1,400	18,700
Los Angeles	IRP Site 35c	8.2	21	130	280	32,200
	Building 720	7.5	22.5	44	260	11,400
	Davis Site	8.0	350	260	400	40,200
McClellan	Capehart Gas Station	5.8	95	54	180	26,700
	PRL T-46	7.4	46	50	5.9	21,300
	Study Area 6	8.0	71	10	590	28,400
McGuire	Tank Farm #2	7.8	120	47	1,100	26,700
	Tank Farm #4	7.4	100	74	150	25,200
	Bulk Fuel Storage	6.1	37	480	217	5,830

Table B-1. Bioventing Initiative Results: Soil Chemical Characterization (Continued)

Air Force Base	Site	pH	Alkalinity (mg/kg)	TKN (mg/kg)	Total Phosphorus (mg/kg)	Iron Content (mg/kg)
Mt. Home	POL Yard	8.4	2,100	76	5.0	21,100
Nellis	Site 27	8.8	1,600	260	170	6,950
	Site 28	8.6	410	100	290	5,800
	Site 44	8.5	800	53	210	6,800
Newark	Facility 27	7.8	370	35	515	15,400
	Facility 89	7.8	460	360	540	16,100
	Facility 14	7.9	320	200	260	16,400
Offutt	Low Point Drain	8.0	330	190	480	7,500
	Building 30	8.7	1,600	250	680	13,700
	Building 406	7.8	360	220	720	18,500
	POL Storage Area	7.9	470	750	600	9,800
Patrick	FTA-2	8.8	220	32	260	440
	BX Service Station	8.4	160	60	290	360
Pease	Bulk Fuel Storage Area	6.6	140	190	730	21,000
	Site 2	5.7	22.5	59	630	39,100
Plattsburgh	Fire Training Area 1	6.6	84	75	<1.0	4,500
	Fire Training Pit 4	6.4	22	36	330	4,500
	Fire Training Area 2&3	7.6	120	49	160	4,200
Pope	IRP Site ST-08	6.7	200	<40	110	3,000
Randolph	Tank 20 Site	8.1	340	230	920	12,400
Robins	UST 173	5.2	<50	90	84	6,000

Table B-1. Bioventing Initiative Results: Soil Chemical Characterization (Continued)

Air Force Base	Site	pH	Alkalinity (mg/kg)	TKN (mg/kg)	Total Phosphorus (mg/kg)	Iron Content (mg/kg)
Robins (continued)	SS10	5.3	<50	46	78	3,600
Shaw	Site FT-01	5.6	22	190	38	4,100
	Site SS-15	5.2	22	20	260	13,900
Tinker	POL Storage Area C	7.3	<50	30	55	3,210
Travis	Fuel Storage Area G	7.4	120	79	220	28,400
	South Gas Station	7.9	120	210	300	22,100
Vandenburg	Service Station	6.9	20	103	100	2,920
	JP-4 Site	6.1	180	57	100	9,700
Westover	Building 7701	6.1	<50	61.5	580	6,835
	Building 7705	6.8	22	200	190	4,900
Wright Patterson	Fire Training Area	7.2	730	680	570	16,200
	Spill Site 2&3	8.1	340	<20	310	6,900

NS Not sampled.

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
AFP 4	FSA-1	Initial	0.36	1.3	12	31	45	29
		Final	BDL	BDL	BDL	BDL	BDL	680
AFP 4	FSA-3	Initial	2.7	9.1	7.1	60	79	140
		Final	BDL	BDL	BDL	BDL	BDL	84
AFP PIKS	ST-35	Initial	BDL	BDL	0.73	1.5	2.2	1,100
		Final	BDL	BDL	BDL	BDL	BDL	130
Battle Creek	Fire Training Area	Initial	0.43	3.0	2.6	17	23	7,200
		Final	BDL	BDL	BDL	0.016	0.016	1,800
Beale	Site 3	Initial	1.5	4.8	3.5	17	26.20	14,000
		Final	BDL	BDL	0.41	1.4	1.81	10,100
Beale	Site 18	Initial	BDL	1.1	2.5	6.0	9.6	23.8
		Final	BDL	BDL	BDL	BDL	BDL	20.9
Beale	Site 11	Initial	1.4	50	24	175	253	17,000
		Final	0.6	0.61	4.4	240	246	5,600
Bolling	Building 18	Initial	BDL	BDL	2.0	1.8	3.80	400
		Final	BDL	BDL	BDL	BDL	BDL	1,600
Bolling	Former Storage Tank Farm	Initial	0.27	8.4	1.5	3.7	13.87	1,800
		Final	0.064	BDL	0.12	0.22	0.40	4,100
Camp Pendleton	Site 1	Initial	0.028	0.072	0.45	0.50	1.05	400
		Final						11.0
Cannon	SWMU 70	Initial	1.5	14	14	53	83	2,700
		Final	BDL	BDL	BDL	BDL	BDL	NR
Cape Canaveral	FTA-2	Initial	4.2	2.6	6.6	13.40	300	14.3
		Final	BDL	BDL	BDL	BDL	BDL	1,100
Cape Canaveral	Facility 1748	Initial	0.58	0.58	2.0	5.7	8.86	17,200
		Final	0.35	0.35	0.35	1.3	2.4	10,500
Cape Canaveral	Facility 44625D	Initial	0.35	0.35	0.35	1.3	2.4	6.4

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Cape Canaveral (continued)	Facility 44625E	Initial	0.40	0.51	0.61	7.1	8.62	9,200
		Initial	BDL	2.0	0.82	2.3	5.12	1,100
		Final	BDL	BDL	BDL	BDL	790	15.8
Charleston	FT-03	Initial	BDL	0.0056	0.0033	0.015	0.02	15
		Initial	0.70	28	2.2	17	47.90	730
		Final	BDL	BDL	BDL	BDL	790	8.1
Davis Monthan	Site SS-41	Initial	3.3	16	14	23	56	530
		Initial	20	100	63	140	323.00	2,700
		Final	BDL	1.1	1.7	8.7	12.40	8.7
Dover	ST-04	Initial	0.90	1.1	1.7	BDL	BDL	BDL
		Initial	BDL	0.33	13	37	50.33	1,200
		Final	BDL	0.25	0.080	0.19	0.52	650
North STF	Site FT40	Initial	BDL	BDL	BDL	0.93	0.93	450
		Initial	BDL	BDL	BDL	BDL	BDL	160
		Final	BDL	BDL	BDL	BDL	BDL	160
Dyess	Site FT41	Initial	0.05	0.05	0.05	0.07	0.22	930
		Initial	BDL	BDL	BDL	BDL	BDL	200
		Final	BDL	BDL	BDL	BDL	BDL	15.4
Edwards	Site 21	Initial	BDL	0.13	1.6	6.5	6.20	110
		Initial	BDL	BDL	BDL	BDL	BDL	23
		Final	BDL	BDL	BDL	BDL	BDL	10
Site 16	Site 43	Initial	0.24	0.29	2.3	12	14.59	24
		Initial	BDL	BDL	BDL	BDL	BDL	5.1
		Final	BDL	BDL	BDL	BDL	BDL	13.3
Eglin	FTA Hurleburt Field	Initial	0.97	14	7.3	48	70.27	9,600
		Initial	BDL	BDL	BDL	BDL	BDL	74
		Final	BDL	BDL	BDL	BDL	BDL	1.65

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Eglin (continued)	Old Eglin FTA	Initial	3.8	7.5	11	32	54.30	4,100
	ST-10	BDL	230	41	340	611.00	4,100	6.9
Eielson	Site 48-E2	Initial	1.4	4.4	11	45	62	5,400
	Site 48-E3	Final	BDL	BDL	0.34	1.4	1.7	1,200
Ellsworth	Area D Bulk Fuel Storage	Initial	8.2	8.9	37	190	244.10	2,800
	Bldg 102 Base Fuel Station	Final	0.842	BDL	1.8	10	12	2,800
Elmendorf	43/45 Valve Pit	Initial	0.18	0.60	0.78	4.3	5.86	11
	ST-61	Final	BDL	BDL	11	44	55	651
ST-71	Initial	BDL	BDL	32	32	BDL	BDL	4.9
	Final	BDL	BDL	0.098	0.22	0.75	1.1	6,000
43/55 Pumphouse	Initial	BDL	BDL	0.019	0.30	0.34	0.66	790
	Final	BDL	BDL	0.001	0.22	0.75	1.1	2,400
FE Warren	Fire Training Pit	Initial	1.7	41	52	241	330	3,900
	Spill Site	Final	BDL	BDL	BDL	BDL	BDL	4.9
Fort Drum	Area 1595	Initial	BDL	BDL	4.8	31	36	400
	Galena	Initial	BDL	BDL	4.1	10	14	700
Saddle Tank Farm	Initial	BDL	BDL	3.4	25	28	15,000	10.6
	Initial	BDL	BDL	0.85	3.7	4.6	270	21.9

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Galena (continued)	Power Plant	Initial	BDL	BDL	BDL	BDL	BDL	97 BDL
		Final	BDL	BDL	BDL	BDL	BDL	22.2 5.8
	Million Gallon Hill	Initial	NS	NS	NS	NS	NS	NS
Hanscom	Campion POL Leak Site	Initial	0.029	0.25	BDL	0.22	0.47	760 12.3
	Building 1639	Initial	0.57	1.5	0.58	4.2	6.85	13 16.6
		Final	0.032	0.57	0.073	0.3	0.98	130 15.3
Hickam	Building 1812	Initial	BDL	0.026	BDL	0.049	0.03	6,500 1,800
		Final	BDL	0.016	BDL	0.023	0.039	4.7 3.1
	Area H	Initial	2.8	5.3	5.5	7.5	21.10	12 24.6
	Area K	Initial	1.1	12	10	19	34.04	20 4.8
		Final	BDL	BDL	BDL	BDL	BDL	24.1 13.7
	Site 2 FSA	Initial	0.6	11	7.4	38	71.74	1,100 1,400
Hill		Final	0.93	3.5	11	12	27	33.7 31.8
	Site 204.1	Initial	0.021	0.16	0.54	5.1	5.82	960 4,500
		Final	BDL	0.01	BDL	0.089	0.099	6.2 7.7
	Site 214.1	Initial	3.3	3.7	5.3	9.1	21	12,100 550
		Final	BDL	BDL	BDL	BDL	BDL	19 NS
	Site 228	Initial	0.64	9.2	7.1	240	256.94	5,800 BDL
	Site 924	Initial	BDL	BDL	BDL	BDL	BDL	6.7 16.7
		Final	BDL	BDL	0.0068	0.029	0.036	BDL BDL

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Hill (continued)	Site 1705	Initial	BDL	BDL	BDL	0.12	0.12	4,400
		Final	BDL	BDL	BDL	4	BDL	600
Site 388	Initial	1.9	43	25	250	320	7,500	8.7
	Final	0.045	0.046	0.54	4	4.6	1,100	6.9
Site 40002	Initial	50	470	160	1,300	1,977.00	28,000	23.2
	Final	32	410	78	1,200	1,700	12,300	27
Site 510.8	Initial	BDL	BDL	BDL	BDL	0.06	5,200	8.1
	Final	BDL	BDL	BDL	0.10	0.10	2,600	6.9
Johnston Atoll Old Fire Training Area	Initial	BDL	0.65	BDL	BDL	0.45	7,700	11.0
	Former POL Tank Farm	Initial	BDL	BDL	3.5	2.5	6.0	13,000
Storage Tanks 260 and 261	Initial	BDL	BDL	15	14	29.00	265	10.7
Keesler SWMU 66	Initial	4.7	35	16	116	171.7	3,300	11.5
	Final	BDL	0.018	BDL	0.0050	0.023	2,500	34.1
AOC A	Initial	0.10	0.039	0.22	0.080	0.44	87	8.4
	Final	BDL	0.0017	BDL	0.0020	0.0037	19	9.0
Kelly Site S-4	Initial	BDL	9.1	BDL	13	20.20	920	21.1
	Final	BDL	0.94	BDL	1.5	2.4	590	22.9
Site FC-2	Initial	BDL	8.0	BDL	22	30.00	1,600	20.1
	Final	0.014	0.13	0.014	0.022	0.18	64	20.5
Site B-2093	Initial	13	130	39	200	382.00	53	18.7
	Initial	BDL	0.0096	BDL	BDL	0.01	86	22.5
Site D-10	Final	BDL	BDL	BDL	BDL	250	250	9.3

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Kirtland	Fire Training Area 13	Initial	BDL	9.1	9.5	57	76	1,800
		Final	BDL	2.2	7.2	38	47	4,800
KI Sawyer	Fire Training Area 14	Initial	BDL	BDL	0.79	3.7	4.49	7,900
		Initial	BDL	40	9.7	27	77.70	1,300
FTA-06	POL Area	Initial	BDL	BDL	0.35	7.8	8.2	2,600
		Final	0.72	7.5	7.8	36	52	6,700
FTA-07		Initial	BDL	0.84	2.2	3.6	11	8,200
		Final	BDL	0.48	1.7	1.9	21	250
Kodiak UCGS	Tank 191	Initial	BDL	0.027	BDL	BDL	0.027	4,000
		Initial	BDL	BDL	BDL	0.43	0.43	4,000
Little Rock	Fire Training Site 1	Initial	BDL	BDL	BDL	BDL	BDL	BDL
		Initial	BDL	BDL	BDL	0.43	0.43	0.43
Los Angeles	Spill Site 18	Initial	BDL	BDL	0.53	0.74	1.27	8.2
		Final	BDL	BDL	BDL	BDL	BDL	BDL
Malmstrom	Building 125	Initial	BDL	BDL	BDL	BDL	BDL	BDL
		Initial	0.0054	0.018	0.35	0.36	0.73	3,700
March	Building 241	Initial	0.031	0.23	1.4	2.3	3.96	4,000
		Initial	BDL	BDL	BDL	BDL	BDL	BDL
McClellan	Gate 3	Initial	0.031	0.23	1.4	2.3	3.96	4,000
		Initial	BDL	BDL	BDL	BDL	BDL	BDL
March	Pumphouse II	Initial	BDL	0.71	1.6	3.7	6.0	240
		Final	BDL	0.067	0.21	0.13	0.41	84.6
McClellan	Bulk POL	Initial	4.7	130	22	120	280	2,700
		Initial	0.011	0.011	0.050	0.16	0.23	1,000
March	IRP Site 35c	Initial	BDL	BDL	BDL	BDL	BDL	BDL
		Final	0.10	0.10	0.10	0.10	0.10	0.10
McClellan	Building 720	Initial	0.10	0.10	0.10	0.10	0.10	0.10
		Initial	BDL	BDL	BDL	BDL	BDL	BDL

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Offutt	Low Point Drain	Initial Final	0.11	1.8	1.0	6.3	9.2	15
	Building 406	Initial Final	2.2 0.048	1.4 0.88	21 0.034	35 1.8	60 2.8	730 1,600
	Building 30	Initial Final	BDL BDL	0.0029 0.0041	BDL BDL	0.014 0.00053	0.02 0.0046	6.6 BDL
	POL Storage Area	Initial Final	0.0042 BDL	0.00082 0.004	0.019 0.004	0.028 0.0073	0.05 0.011	4.3 5.5
Patrick	FTA-2	Initial Final	3.4 BDL	26 0.034	190 BDL	920 BDL	1,100 0.034	930 6,500
	BX Service Station	Initial Final	4.5 0.60	0.72 0.067	3.0 0.07	18 0.2	26 0.94	10,500 63
Pease	Bulk Fuel Storage Area	Initial Final	0.33 BDL	1.1 BDL	5.2 BDL	15 BDL	21.63 BDL	310 210
	Site 2	Initial	0.024	3.2	0.057	0.68	3.96	17
Plattsburgh	Fire Training Area 2&3	Initial Final	BDL BDL	0.026 0.94	0.0042 1.5	0.14 2.4	0.17 2.4	5,200 5,200
	Fire Training Pit 4	Initial	0.85	0.85	16	80	97.70	4,500
	Fire Training Area 1	Initial	1.9	30	20	135	186.80	2,500
Pope	Site ST-08	Initial	BDL	BDL	BDL	BDL	BDL	3,200
Randolph	Tank 20 Site	Initial	BDL	4.7	3.3	33	41.00	230
Robins	UST 173	Initial Final	BDL BDL	0.0056 0.82	0.11 0.73	1.0 1.6	1,900 340	11.8 14.3 11.2

Table B-2. Bioventing Initiative Results: Average BTEX and TPH Soil Concentrations (Continued)

Air Force Base	Site	Time	Soil Analysis					
			Benzene (mg/kg)	Toluene (mg/kg)	Ethylbenzene (mg/kg)	Total Xylenes (mg/kg)	Total BTEX (mg/kg)	TPH (mg/kg)
Robins (continued)	SS10	Initial	0.28	20	14	76	110.02	3,100
		Final	7.3	21	21	100	150	3,600
Shaw	Site FT-01	Initial	0.31	1.7	3.6	3.2	8.81	4,500
		Initial	1.7	3.8	7.1	36	48.60	2,400
Tinker	POL Storage Area C	Initial	1.9	45	53	83	138.59	2,300
		Final	0.0012	0.0015	0.0049	0.037	0.045	BDL
Travis	Fuel Storage Area G	Initial	0.26	0.69	9.1	13	22.72	64
		Final	BDL	BDL	13	88	100	5,400
Vandenburg	South Gas Station	Initial	4.6	22	13	71	110.60	20
		Initial	BDL	5.4	4.9	46	56.30	230
Westover	JP-4 Site	Initial	0.44	2.0	1.8	6.4	11	6.2
		Initial	BDL	BDL	BDL	BDL	BDL	NR
Wright Patterson	Building 7701	Initial	BDL	BDL	BDL	BDL	BDL	4.7
		Final	BDL	BDL	BDL	BDL	BDL	NR
	Building 7705	Initial	BDL	0.47	BDL	0.73	1.22	22
		Final	BDL	0.20	0.087	0.35	0.64	BDL
	Fire Training Area	Initial	BDL	0.026	0.0028	0.015	0.04	19.5
		Final	BDL	BDL	BDL	BDL	BDL	17.0
	Spill Site 2&3	Initial	BDL	0.016	BDL	0.0054	0.02	BDL
		Final	BDL	BDL	BDL	BDL	BDL	4.2

BDL Below detection limit.

NR Not reported.

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
AFP 4	FSA-1	Initial	BDL	BDL	21	19	40.96
		Final	0.24	0.094	0.23	0.67	1.2
FSA-3		Initial	BDL	BDL	6.4	12.5	19.03
		Final	0.28	0.21	0.65	0.93	2.1
AP PIKS	ST-35	Initial	8.2	8.8	6.5	14	37.50
		Final	BDL	0.004	0.026	0.070	0.10
Battle Creek	Fire Training Area	Initial	50	18	2.8	11	81.40
		Final	BDL	0.0027	BDL	BDL	0.0027
Beale	Site 3	Initial	2.3	1.9	0.71	2.3	3.74
		Final	0.27	0.60	0.87	2.0	3.7
Site 18		Initial	11	1.6	2.0	1.8	16.40
		Final	4.7	BDL	0.80	1.7	7.2
Site 11		Initial	350	530	37	300	1,215.00
		Final	1.3	13	7.3	180	200
Bolling	Building 18	Initial	0.056	0.18	0.30	0.74	1.28
		Final	BDL	0.0033	0.016	0.058	0.077
	Former Storage Tank Farm	Initial	0.21	7.9	4.0	5.2	17.31
		Final	BDL	BDL	BDL	BDL	12,700

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

		Soil Gas Analysis						
Air Force Base	Site	Time	Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)	TPH (ppmv)
Camp Pendleton	Site 131151	Initial	0.34	1.2	1.2	3.4	6.1	460
Cannon	SWMU 70	Initial	30	18	7.4	23	78	9,000
Cape Canaveral	FTA-2	Initial	1.5	0.11	3.6	4.8	10.01	3,900
		Final	0.016	0.011	0.026	0.071	0.12	210
	Facility 1748	Initial	1.5	0.021	3.4	3.3	8.22	750
	Facility 44625D	Initial	0.36	0.20	0.015	1.6	2.18	397
Charleston	Facility 44625E	Initial	0.059	0.53	0.33	2.2	3.12	303
	FT-03	Initial	BDL	BDL	0.061	0.11	0.17	410
		Final	BDL	BDL	0.0013	BDL	0.0013	6.7
	ST-27	Initial	126	557	81	253	1,017.00	118,333
Davis Monthan	Site SS-41	Initial	0.30	0.30	4.87	9.8	15.27	19,667
	Site 35	Initial	693	681	93	153	1,620.00	46,098
	Site 36	Initial	583	665	118	254	1,620.00	39,667
	ST-04	Initial	65	44	13.4	47	169.40	33,500
Dyess	North STF	Initial	5.4	4.8	2.5	5.4	18	6,150
	Site FT40	Initial	0.015	0.08	0.011	0.042	0.15	49
		Final	BDL	0.002	BDL	0.012	0.014	1.5
	Site FT41	Initial	0.016	0.19	0.14	0.26	0.61	320
		Final	BDL	0.018	BDL	0.013	0.031	1.6

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

			Soil Gas Analysis					
Air Force Base	Site	Time	Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)	TPH (ppmv)
Edwards	Site 21	Initial	190	16	12	38	253.00	49,000
		Final	0.26	0.24	0.72	1.7	2.9	220
	Site 16	Initial	230	26	20	89	365.00	63,000
		Final	0.8	0.83	2	5.3	8.9	575
Site 43	Initial	BDL	0.0088	0.091	0.48	0.59	380	
	Final	BDL	0.006	0.012	0.11	0.13	0.95	
	FTA Hurlebur Field	Initial	36	46	12	78	172.00	17,667
		Initial	146	179	29	120	474.00	16,000
Eielson	ST-10	Initial	567	150	4.0	43	764.00	48,000
		Final	BDL	1.6	BDL	4.4	6.0	2,100
	Site 48-E2	Initial	66	51	3.4	12	132.40	6,000
		Final	0.32	2.1	2.5	26	31	1,200
Ellsworth	Site 48-E3	Initial	4.6	0.25	0.45	1.1	6.40	1,866
		Final	BDL	BDL	1.8	4.2	6.0	610
	Area D Bulk Fuel Storage	Initial	140	13	12.9	30	128.50	35,000
		Final	0.0091	0.017	2	8.4	10	780
	Bldg 102 Base Fuel Station	Initial	320	48	6.7	39	416.70	79,000
		Final	BDL	0.074	6.7	32	39	840
	Elmendorf	Initial	13	80	7.5	28	128.50	13,550
		Final						

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
Elmendorf (continued)	ST-61	Initial	0.053	0.32	0.4	1.1	1.87
		Final	BDL	0.22	0.95	1.3	2.5
	ST-71	Initial	BDL	BDL	0.22	1.12	1.35
		Final	BDL	0.004	0.032	0.033	0.069
43/55 Pumphouse	Initial	19	64	15	50	50	150
		Final	0.87	0.86	5.1	33	40
	Fire Training Pit	Initial	0.92	2.5	1.9	5.1	10.42
		Initial	180	28	24	110	348.00
FE Warren	Spill Site	Final	BDL	0.012	0.049	0.27	0.33
		Initial	BDL	7.2	2.7	16	26
	Area 1595	Initial	40	8.3	2.7	6.4	57.40
	Saddle Tank Farm	Initial	0.059	1.1	3.8	3.5	8.5
Fort Drum	Power Plant	Final	0.060	BDL	1.4	3.2	4.7
		Initial	6.4	5.7	0.64	2.5	15
	Million Gallon Hill	Final	BDL	BDL	3.5	10	14
	Campion POL Leak Site	Initial	0.022	0.040	0.054	0.22	0.34
Galena	Building 1639	Initial	8.1	10	3.6	17	38.70
		Final	8.3	9	0.47	5.5	23
	Building 1812	Initial	NS	NS	NS	NS	NS

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
Hickam	Area H	Initial	BDL	BDL	28	22	56.80
		Final	BDL	BDL	0.0067	0.0053	0.012
	Area K	Initial	85	BDL	22	48	155.70
		Final	BDL	BDL	2	5.3	7.3
Site 2 FSA	Initial	16	29	12	40	97.00	13,800
		Final	BDL	BDL	7.4	18	25
	Initial	0.026	0.11	0.085	0.39	0.61	220
		Final	0.0025	0.0047	BDL	0.0023	0.0095
Hill	Site 204.1	Initial	0.010	0.039	0.26	0.26	0.57
		Final	BDL	BDL	0.036	0.18	0.22
	Site 214.1	Initial	0.83	2.2	0.85	4.6	8.48
		Final	0.021	0.029	0.016	0.13	0.20
Site 228	Initial	34	80	3.6	44	150	20
		Final	0.0025	0.0045	BDL	BDL	0.0070
	Initial	0.012	0.019	0.011	0.053	0.10	44
		Final	BDL	0.0025	0.0017	0.035	0.039
Site 388	Initial	175	180	8.9	80	440.90	26,000
		Final	2.3	97	25	260	380
	Initial	BDL	280	12	110	303.59	11,100
Site 40002	Initial						

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
Hill (continued)	Site 40002	Final	1.2	140	9.7	150	300
	Site 510.8	Initial	BDL	0.18	0.06	0.43	0.69
		Final	BDL	BDL	0.065	0.20	0.27
Johnston Atoll	Old Fire Training Area	Initial	0.016	0.47	0.95	2.8	4.24
	Former POL Tank Farm	Initial	0.1	0.11	3.03	2.3	5.54
	Storage Tanks 260&261	Initial	0.059	0.066	1.5	2.0	3.63
Keesler	SWMU 66	Initial	23	44	4.5	20	91.50
	AOC A	Initial	1,100	550	51	120	1,800
		Final	42	220	53	230	550
Kelly	Site S-4	Initial	200	22	23	20	265.00
		Final	0.041	0.88	0.3	0.63	1.9
	Site FC-2	Initial	38	15	18	15	86.00
Kirtland	Site B-2093	Initial	175	323	25	87	610.00
	Site D-10	Initial	0.003	0.051	0.18	0.34	0.57
		Final	BDL	0.016	0.003	0.015	0.034
	Fire Training Area 13	Initial	19	56	8.3	34	117.30
		Final	0.011	BDL	0.1	0.56	0.67
	Fire Training Area 14	Initial	NS	NS	NS	NS	NS

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
K.I. Sawyer	POL Area	Initial	393	178	9.1	15	595.10
	FTA-06	Initial	8.6	7.2	0.53	2.6	19
		Final	0.16	0.13	0.23	0.68	1.2
	FTA-07	Initial	3.1	6.2	0.40	2.2	12
		Final	1.2	10	4.0	22	37
	Kodiak USCG	Initial					820
Little Rock	Fire Training Site 1	Initial	NS	NS	NS	NS	710
	Spill Site 18	Initial	BDL	BDL	8.7	16	25
		Initial	0.026	0.026	0.089	0.2	0.34
Los Angeles	Building 125	Initial					2,200
	Building 241	Initial	0.065	0.31	0.59	0.91	1.88
	Gate 3	Initial	0.026	0.026	0.57	1.17	1.79
Malmstrom	Pumphouse 2	Initial	6.6	BDL	9.1	12	28
		Final	BDL	BDL	0.15	0.28	0.43
	POL SA	Initial	BDL	12	12	38	62
March	IRP Site 35c	Initial	0.035	0.035	0.41	0.67	1.15
	Building 720	Initial	NS	NS	NS	NS	NS
	Davis Site	Initial	0.0053	0.004	0.39	0.67	1.07
McClellan		Final	BDL	0.0045	0.0050	0.10	0.11
							230

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
McClellan (continued)	PRJ T-46	Initial	0.18	0.18	3.3	1.84	5.50
		Final	0.34	3.0	2.8	6.0	12
Study Area 6		Initial	165	124	13	81	383.00
		Final	3.8	7.2	4.8	36	52
Tank Farm #2		Initial	0.68	28	7.9	30	66.58
		Final	BDL	0.38	7.0	13	20
Tank Farm #4		Initial	0.11	0.11	5.3	5.7	11.22
		Final	BDL	BDL	0.046	0.15	0.20
McGuire	Bulk Fuel Storage	Initial	73	190	17	58	340
		Final	10	22	5.1	45	82
Mt. Home	POL Yard	Initial	550	25	560	270	1,400
		Initial	543	372	37	100	1,052.00
Nellis	Site 27	Initial	6.0	14	5.1	16	41
		Final	520	547	55	185	1,307.00
Newark	Facility 27	Initial	203	753	68	377	1,401.00
		Initial	0.019	0.023	0.0097	0.11	0.16
	Facility 89	Initial	0.0072	0.015	0.0045	0.0088	0.04
		Initial	NS	NS	NS	NS	NS
	Offutt	Initial	88	153	29	77	347.00
		Low Point Drain					29.750

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
Offutt (continued)	Building 30	Initial	BDL	BDL	BDL	1.6	311.00
		Final	BDL	BDL	BDL	BDL	8,200
	Building 406	Initial	290	BDL	44	51	BDL
		Final	BDL	BDL	6.5	28	170
POL Storage Area	Initial	67	11	4	9.5	382.92	18,300
		Final	BDL	BDL	BDL	35	2,300
	Final	BDL	BDL	BDL	BDL	304.00	13,500
		Initial	BDL	BDL	1.5	5.2	BDL
Patrick	FTA-2	Initial	BDL	BDL	BDL	0.36	860
		Final	0.048	0.003	0.024	0.058	0.13
	BX Service Station	Initial	BDL	44	24	200	68
		Final	0.027	0.002	0.0045	0.23	7.18
Pease	Initial	117	9.7	18	22	166.70	62,000
		Final	BDL	BDL	BDL	BDL	4.3
	Initial	4.4	10	2.1	14	0.26	48,000
		Final	BDL	0.016	0.0045	0.013	BDL
Plattsburgh	Fire Training Pit 2&3	Initial	11	18	24	82	30.50
		Final	BDL	BDL	BDL	BDL	4,312
	Initial	6.01	20	4.2	15	0.034	9.9
		Final	BDL	BDL	BDL	BDL	7,200
Pope	Initial	Site ST-08	BDL	25	4.0	10	140
		Final	BDL	BDL	BDL	BDL	45.21
	Initial	Tank 20 Site	16	0.53	6.1	18	19,348
		Final	BDL	BDL	BDL	BDL	3,800
Randolph	UST 173	Initial	0.0013	0.028	0.17	1.04	50
		Final	BDL	BDL	BDL	BDL	206

Table B-3. Bioventing Initiative Results: BTEX and TPH Soil Gas Concentrations (continued)

Air Force Base	Site	Time	Soil Gas Analysis				
			Benzene (ppmv)	Toluene (ppmv)	Ethylbenzene (ppmv)	Total Xylenes (ppmv)	Total BTEX (ppmv)
Robins (continued)	UST 173	Final	0.086	0.011	BDL	0.016	0.11
		Initial	270	109	16	84	479.00
	SS10	Final	57	40	15	67	180
Shaw	Site SS-15	Initial	210	200	32	120	560
		Initial	53	100	11	36	202.00
Tinker	POL Storage Area C	Final	0.018	0.022	0.73	1	1.8
		Initial	1,300	550	100	97	2,048.00
Travis	Fuel Storage Area G	Final	7.1	11	6.4	31	56
		Initial	1,650	1,125	61	240	3,076.00
Vandenburg	South Gas Station	Initial	160	84	28	139	411.00
		Initial	NS	NS	NS	NS	NS
Westover	JP-4 Site	Initial	NS	NS	NS	NS	NS
		Final	610	BDL	0.13	0.031	610
Wright Patterson	Building 7701	Initial	BDL	BDL	0.12	0.087	0.23
		Final	BDL	0.0093	0.0063	0.023	0.039
	Building 7705	Initial	0.23	0.42	0.21	0.29	1.15
		Initial	0.07	2.59	1.92	6.76	11.34
	Fire Training Area	Initial	0.07	2.59	1.92	6.76	11.34
		Spill Site 2&3	2,398				

NS Not sampled.
BDL Below detection limit.

Table B-4. In Situ Respiration Test Results at Bioventing Initiative Sites

Air Force Base	Site	Initial		6-month		1-year	
		%/hr	m/kg-day	%/hr	mg/kg-day	%/hr	mg/kg-day
AFP 4	FSA-1	0.32	5.22	0.058	0.95	0.059	0.96
	FSA-3	0.91	14.85	0.36	5.88	0.54	8.81
	ST-35	0.52	8.49	0.17	2.77	0.33	5.39
Battle Creek	Fire Training Area	0.39	6.36	0.12	1.96	0.16	2.61
Beale	Site 3	0.14	2.28	0.043	0.70	0.016	0.26
	Site 18	0.74	12.08	0.078	1.27	0.069	1.13
	Site 11	0.12	1.96	0.031	0.51	0.033	0.54
Boeing	Building 18	0.11	1.80	0.011	0.18	0.080	1.31
	Former Storage Tank Farm	1.4	22.85	1.5	24.48	0.98	15.99
	Camp Pendleton Site 1	0.021	0.34	Not conducted	Not conducted	Not conducted	Not conducted
Cannon	SW/MU 70	0.53	8.65	Not conducted	Not conducted	Not conducted	Not conducted
	FTA-2	0.18	2.94	Not conducted	Not conducted	Not conducted	Not conducted
	Facility 1748	0.16	2.61	Not conducted	Not conducted	Not conducted	Not conducted
Cape Canaveral	Facility 44625D	0.39	6.36	Not conducted	Not conducted	Not conducted	Not conducted
	Facility 44625E	0.17	2.77	Not conducted	Not conducted	Not conducted	Not conducted
	FT-03	0.54	8.81	0.0059	0.10	0.084	1.37
Charleston	Site SS-41	0.38	6.20	Not conducted	Not conducted	Not conducted	Not conducted
	Site 35	0.009	0.15	Not conducted	Not conducted	Not conducted	Not conducted
	Site 36	0.078	1.27	Not conducted	Not conducted	Not conducted	Not conducted
Dover	ST-04	0.18	2.94	Not conducted	Not conducted	Not conducted	Not conducted
	North STF	0.30	4.90	Not conducted	Not conducted	Not conducted	Not conducted
	Dyess Site FT40	0.010	0.16	Not conducted	Not conducted	Not conducted	Not conducted

Table B-4. In Situ Respiration Test Results at Bioventing Initiative Sites (continued)

Air Force Base	Site	Initial		6-month		1-year	
		%/hr	m/kg-day	%/hr	mg/kg-day	%/hr	mg/kg-day
Dyess (continued)	Site F141	Not conducted					
Edwards	Site 21	0.16	2.61	0.016	0.26	0.23	3.75
	Site 16	0.031	0.51	0.0051	0.08	0.059	0.96
	Site 43	0.033	0.54	0.0060	0.10	0.019	0.31
Eglin	FTA Hurleburgt Field	0.18	2.94	Not conducted	Not conducted	Not conducted	Not conducted
	Old Eglin FTA	0.18	2.94	Not conducted	Not conducted	Not conducted	Not conducted
Eielson	ST-10	0.29	4.73	0.22	3.59	0.10	1.63
	Site 48-E2	0.18	2.94	0.046	0.75	0.11	1.80
	Site 48-E3	Not conducted	Not conducted	0.067	1.09	0.11	1.80
Ellsworth	Area D Bulk Fuel Storage	1.1	17.95	0.068	1.11	0.074	1.21
	Bldg 102 Base Fuel Station	0.034	0.55	0.0096	0.16	0.0056	0.09
Elmendorf	43/45 Pumphouse	0.51	8.32	0.09	1.47	0.32	5.22
	ST-61	0.38	6.20	0.072	1.18	0.44	7.18
	ST-71	0.056	0.91	0.015	0.24	0.06	0.98
	43/55 Pumphouse	0.34	5.55	0.0066	0.11	0.16	2.61
FE Warren	Fire Training Pit	0.62	10.12	Not conducted	Not conducted	Not conducted	Not conducted
	Spill Site	1.4	22.85	0.052	0.85	0.018	0.29
Galena	Saddle Tank Farm	1.05	17.14	Not conducted	Not conducted	Not conducted	Not conducted
	Power Plant	1.4	22.85	Not conducted	Not conducted	0.59	9.63
	Million Gallon Hill	0.44	7.18	Not conducted	Not conducted	0.11	1.80

Table B-4. In Situ Respiration Test Results at Bioventing Initiative Sites (continued)

Air Force Base	Site	Initial		6-month		1-year	
		%/hr	m/kg-day	%/hr	mg/kg-day	%/hr	mg/kg-day
Galena (Continued)	Campion POL Leak Site	0.99	16.16	Not conducted	Not conducted	Not conducted	Not conducted
Hanscom	Building 1639	0.78	12.73	0.26	4.24	0.048	0.78
	Building 1812	Not conducted	Not conducted	0.036	0.59	Not conducted	Not conducted
Hickam	Area H	0.71	11.59	0.093	1.52	0.012	0.20
	Area K	1.2	19.58	0.45	7.34	0.38	6.20
	Site 2 FSA	0.6	9.79	0.27	4.41	0.53	8.65
Hill	Site 204.1	0.98	15.99	0.057	0.93	0.096	1.57
	Site 214.1	0.31	5.06	0.015	0.24	0.015	0.24
	Site 228	0.54	8.81	0.031	0.51	0.059	0.96
	Site 924	0.56	9.14	0.043	0.70	0.007	0.12
	Site 1705	Not conducted					
	Site 388	0.42	6.85	0.090	1.47	0.39	6.36
	Site 40002	0.22	3.59	0.016	0.26	0.083	1.35
	Site 510.8	0.022	0.36	0.021	0.34	0.091	1.49
Johnston Atoll	Old Fire Training Area	0.42	6.85	Not conducted	Not conducted	0.44	7.2
	Former POL Tank Farm	0.24	3.92	Not conducted	Not conducted	0.22	3.5
	Storage Tanks 260 and 261	0.64	10.44	Not conducted	Not conducted	0.23	3.7
Keesler	SWMU 66	0.65	10.61	0.41	6.69	0.60	9.79
	AOC A	0.081	1.32	0.097	1.58	0.083	1.35
Kelly	Site S-4	2.4	39.17	0.28	4.57	0.11	1.80

Table B-4. In Situ Respiration Test Results at Bioventing Initiative Sites (continued)

Air Force Base	Site	Initial		6-month		1-year	
		%/hr	mg/kg-day	%/hr	mg/kg-day	%/hr	mg/kg-day
Kelly (Continued)	Site FC-2	1.9	31.01	0.72	11.75	0.58	9.47
	Site D-10	1.1	17.95	0.057	0.93	0.070	1.14
Kirtland	Fire Training Area 13	0.061	1.00	0.012	0.20	0.0083	0.13
	Fire Training Area 14	0.0055	0.09	0.0043	0.07	Not conducted	Not conducted
KI Sawyer	POL Area	0.11	1.80	0.11	1.80	0.16	2.61
	FTA-06	0.13	2.12	0.047	0.77	0.029	0.47
	FTA-07	0.074	1.21	0.021	0.34	0.012	0.20
Little Rock	Spill Site 18	2.04	33.29	Not conducted	Not conducted	Not conducted	Not conducted
	Building 125	0.33	5.39	Not conducted	Not conducted	Not conducted	Not conducted
Los Angeles	Building 241	0.25	4.08	Not conducted	Not conducted	Not conducted	Not conducted
	Gate 3	0.27	4.41	Not conducted	Not conducted	Not conducted	Not conducted
	Pumphouse II	3.2	52.22	0.29	4.73	Not conducted	Not conducted
Malmstrom	POL SA	1.1	17.95	0.34	5.55	0.25	4.08
	IRP Site 35c	0.29	4.73	Not conducted	Not conducted	Not conducted	Not conducted
March	Davis Site	0.37	6.04	0.12	1.96	0.50	8.16
	PRL T-46	0.91	14.85	0.19	3.10	0.37	6.04
McClellan	Study Area 6	0.32	5.22	0.016	0.26	0.11	1.80
	Tank Farm #2	0.31	5.06	0.030	0.49	0.064	1.04
McGuire	Tank Farm #4	0.33	5.39	0.011	0.18	0.099	1.62
	Bulk Fuel Storage	1.2	19.58	0.28	4.57	0.72	11.75
Mt. Home	POL Yard	0.32	5.22	Not conducted	Not conducted	Not conducted	Not conducted

Table B-4. In Situ Respiration Test Results at Bioventing Initiative Sites (continued)

Air Force Base	Site	Initial		6-month		1-year	
		%/hr	m/kg-day	%/hr	mg/kg-day	%/hr	mg/kg-day
Nellis	Site 27	0.048	0.78	0.0035	0.06	0.031	0.51
	Site 28	0.21	3.43	0.038	0.62	0.016	0.26
	Site 44	0.69	11.26	0.028	0.46	0.022	0.36
Newark	Facility 27	0.26	4.24	Not conducted	Not conducted	0.015	0.24
	Facility 89	0.021	0.34	0.0096	0.16	0.021	0.34
	Low Point Drain	0.86	14.04	Not conducted	Not conducted	Not conducted	Not conducted
Offutt	Building 406	5.6	91.39	0.33	5.39	0.26	4.24
	Building 30	4.9	79.97	0.051	0.83	0.039	0.64
	POL Storage Area	0.1	1.63	Not conducted	Not conducted	0.46	7.51
Patrick	FTA-2	0.34	5.55	0.41	6.69	0.33	5.39
	BX Service Station	0.16	2.61	0.21	3.43	0.028	0.46
	Bulk Fuel Storage Area	3.57	58.26	Not conducted	Not conducted	Not conducted	Not conducted
Plattsburgh	Fire Training Area 2&3	0.84	13.71	0.17	2.77	0.094	1.53
	Fire Training Pit 4	0.20	3.26	Not conducted	Not conducted	Not conducted	Not conducted
	Tank 20 Site	0.41	6.69	0.15	2.45	0.28	4.57
Robins	UST 173	0.029	0.47	0.0023	0.04	0.013	0.21
	SS10	0.18	2.94	0.031	0.51	0.020	0.33
	Site FT-01	0.43	7.02	Not conducted	Not conducted	Not conducted	Not conducted
Shaw	Site SS-15	0.16	2.61	Not conducted	Not conducted	Not conducted	Not conducted
	POL Storage Area C	0.18	2.94	0.038	0.62	0.056	0.91
	Fuel Storage Area G	3.6	58.75	0.79	12.89	0.86	14.04

Table B-4. In Situ Respiration Test Results at Bioventing Initiative Sites (continued)

Air Force Base	Site	Initial		6-month		1-year	
		%/hr	m/kg-day	%/hr	mg/kg-day	%/hr	mg/kg-day
Travis (Continued)	South Gas Station	2.47	40.31	Not conducted	Not conducted	Not conducted	Not conducted
Vandenburg	Service Station	0.24	3.92	Not conducted	Not conducted	Not conducted	Not conducted
Westover	Building 7701	0.33	5.39	0.0098	0.16	0.052	0.85
	Building 7705	0.12	1.96	Not conducted	Not conducted	0.05	0.82
Wright Patterson	Fire Training Area	0.19	3.10	Not conducted	Not conducted	Not conducted	Not conducted
	Spill Site 2&3	0.26	4.24	Not conducted	Not conducted	Not conducted	Not conducted